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(54) ORGANIC MATTER COATED STEEL SHEET EXCELLENT IN CORROSION RESISTANCE, AND ITS PRODUCTION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic matter coated steel sheet safe and harmless in production process and in use and further capable of obtaining excellent corrosion resistance.

SOLUTION: The surface of a galvanized steel sheet or an aluminum-plated steel sheet is, as a first layer film, provided with a composite oxide film containing (α) oxide fine grains, (β) phosphoric acid and/or a phosphoric compound and (γ) one or more kinds of metals selected from among Mg, Mn and Al, and the upper part thereof is, as a second layer film, provided with an organic film containing a reaction product (X) between a film forming organic resin (A) and an active hydrogen-containing compound (B) in which a part or the whole of the compound is composed of a hydrazine derivative (C) containing active hydrogen and any rust

preventive addition component (Y) of one or more kinds of organic compounds selected from among (a) Ca ion exchanged silica and phosphate, (b) Ca ion exchanged silica, phosphate and silicon oxide, (c) a calcium compound and silicon oxide, (d) a calcium compound, phosphate and silicon oxide, (e) molybdate and (f) triazoles, thiols, thiadiazoles, thiazoles and thiurams.

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CLAIMS

[Claim(s)]

[Claim 1] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of either of following (a) - (f) is included. (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, Phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, Phosphate and silicon oxide (e) molybdate (f) triazoles The content of the sum total of one or more sorts of organic compound aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 2] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (g), and (h) is included. (e) The content of the sum total of molybdate (g) calcium, lime compound (h) phosphate, and/or the silicon oxide aforementioned rust-proofing addition component (Y) is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 3] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (e) and the rust-proofing addition component (Y) of (i) are included. The content of the sum total of the (e) molybdate (i) calcium ion-exchange silica aforementioned rust-proofing addition component (Y) is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section

(solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 4] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (f), (g), and (h) is included. (f) triazoles Thiols, thiadiazole, and thiazoles The content of the sum total of one or more sorts of organic compound (g) calcium chosen from thiurams, lime compound (h) phosphate, and/or the silicon oxide aforementioned rust-proofing addition component (Y) receives the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat which is the 1 - 100 weight section (solid content), and whose thickness is 0.1-5 micrometers.

[Claim 5] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (f) and the rust-proofing addition component (Y) of (i) are included. (f) triazoles The content of the sum total of one or more sorts of (organic compound i) calcium ion-exchange silica aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 6] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (e) and the rust-proofing addition component (Y) of (f) are included. (e) molybdate (f) triazoles The content of the sum total of one or more sorts of organic compound aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 7] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (f), (g), and (h) is included. (e) Molybdate (f) triazoles, thiols, and thiadiazole Thiazoles The content of the sum total of one or more sorts of organic compound (g) calcium chosen from thiurams, lime compound (h) phosphate, and/or the silicon

oxide aforementioned rust-proofing addition component (Y) receives the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat which is the 1 - 100 weight section (solid content), and whose thickness is 0.1-5 micrometers.

[Claim 8] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, as the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (f), and (i) is included. (e) molybdate (f) triazoles The content of the sum total of one or more sorts of (organic compound i) calcium ion-exchange silica aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[Claim 9] The organic covering steel plate the organic coat excelled [steel plate] in the corrosion resistance according to claim 1, 2, 3, 4, 5, 6, 7, or 8 characterized by the content of this solid lubricant (Z) being 1 - 80 weight section (solid content) to the said (resultant X) 100 weight section (solid content) including solid lubricant (Z) further.

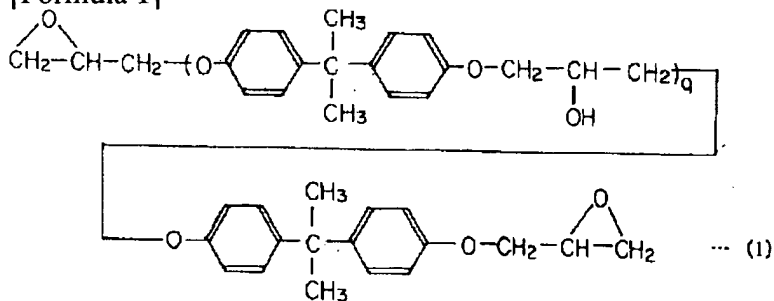
[Claim 10] The organic covering steel plate excellent in the corrosion resistance according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 to which coat formation organic resin (A) is characterized by being epoxy group content resin (D).

[Claim 11] The organic covering steel plate excellent in the corrosion resistance according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 characterized by the hydrazine derivative (C) which has active hydrogen being the triazole compound which has the pyrazole compound and/or active hydrogen which have active hydrogen.

[Claim 12] the hydrazine derivative (C) which has active hydrogen -- the inside of an active hydrogen compound (B) -- 10 - 100-mol % -- the organic covering steel plate excellent in the corrosion resistance according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11 characterized by being contained.

[Claim 13] The organic covering steel plate excellent in the corrosion resistance according to claim 10, 11, or 12 characterized by being the epoxy resin in which epoxy group content resin (D) is shown by the following formula (1).

[Formula 1]



(q : 0 ~ 5 0)

[Claim 14] The organic covering steel plate excellent in corrosion resistance given in claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 characterized by the component (alpha) contained in a multiple oxide coat being silicon oxide, or 13.

[Claim 15] The organic covering steel plate excellent in corrosion resistance given in claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 13 characterized by a multiple oxide coat containing organic resin further, or

14.

[Claim 16] A multiple oxide coat A component (alpha), the component (beta) in the amount of P2O5 conversions, and Mg, The sum total coating weight of the component (gamma) in the amount of metal conversions of Mn and aluminum is 6 - 1000 mg/m². An organic coat is the organic covering steel plate excellent in corrosion resistance given in claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 characterized by coating weight being two or more 0.1 g/m and less than two 0.5 g/m, or 15.

[Claim 17] It is the manufacture approach of claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 or an organic covering steel plate given in 16. On the front face of a zinc system plating steel plate or an aluminum system plating steel plate A (b) oxide particle, (**) -- a phosphoric acid and/or a phosphoric-acid compound, and the metal ion of the Mg (Ha), Mn, or the aluminum -- One sort or two sorts or more which are chosen from the groups which consist of the water-soluble ion containing at least one sort in said metal, a compound containing at least one sort in said metal, and a conjugated compound containing at least one sort in said metal, It contains. The mol concentration of said addition component (b), the sum total mol concentration of 2OP5 conversion of said addition component (b), $/(Ha) = 0.1-20$ and the processing liquid adjusted so that a mole ratio $(Ha) / (b) = 0.1-1.5$ might be satisfied are applied. the sum total mol concentration of the amount conversion of metals of said metal of said addition component (Ha) -- mole-ratio (**) -- The multiple oxide coat whose thickness is 0.005-3 micrometers is formed in a plating steel plate front face by carrying out stoving after an appropriate time. Subsequently The manufacture approach of an organic covering steel plate excellent in the corrosion resistance characterized by forming the organic coat whose thickness is 0.1-5 micrometers by applying and carrying out stoving of the coating constituent for organic coat formation to the upper part.

[Claim 18] The manufacture approach of an organic covering steel plate excellent in the corrosion resistance according to claim 17 characterized by addition component (b) in the processing liquid for multiple oxide coat formation being silicon oxide.

[Claim 19] The manufacture approach of an organic covering steel plate excellent in the corrosion resistance according to claim 17 or 18 to which the processing liquid for multiple oxide coat formation is characterized by containing organic resin further.

[Claim 20] On a plating steel plate front face, a component (alpha), the component (beta) in the amount of P2O5 conversions, and Mg, The sum total coating weight of the component (gamma) in the amount of metal conversions of Mn and aluminum forms the multiple oxide coat of 6 - 1000 mg/m². The manufacture approach of an organic covering steel plate excellent in the corrosion resistance according to claim 17, 18, or 19 characterized by coating weight forming a two or more 0.1 g/m and less than two 0.5 g/m organic coat in the upper part of this multiple oxide coat.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Since it is adapted for environmental problems , such as volatilization , elution , etc. of the effect on the operator and user who deal with a product about the optimal organic covering steel plate for an automobile , household electric appliances , a building materials application , etc. , the cure against waste water treatment at the time of manufacture , and the harmful matter from the product under an operating environment further , this invention relates to the environmental ecad surface treated steel sheet which does not contain heavy metal , such as chromium , lead , cadmium , and mercury , at all in the time of manufacture , and a product .

[0002]

[Description of the Prior Art] From the former, the steel plate with which chromate treatment with the processing liquid which used a chromic acid, dichromic acid, or its salts as the major component was performed is broadly used for the front face of a zinc system plating steel plate or an aluminum system plating steel plate at the steel plate for home electronics, the steel plate for building materials, and the steel plate for automobiles in order to raise corrosion resistance (white-rust-proof, rust-proof nature). This chromate treatment is the economical art which can be performed comparatively easily [excel in corrosion resistance and] .

[0003] Although chromate treatment uses the hexavalent chromium which is the public nuisance regulation matter, neither an environment nor the body is substantially polluted by hexavalent chromium from this hexavalent chromium being processed with a closed system in down stream processing, and it being returned and collected completely, and not being emitted to a nature, and chromium elution out of a chromate film being mostly made to zero according to the sealing operation by the organic coat. However, the motion which is going to reduce use of heavy metal including hexavalent chromium independently from the latest global environment problems is increasing. Moreover, when the shredder dust of an abandonment product is abandoned, in order to make it not pollute an environment, or it does not include heavy metal as much as possible in a product, the motion which is going to reduce this has also started.

[0004] Since it is such, in order to prevent generating of the white rust of a zinc system plating steel plate, many pollution-free processing techniques by chromate treatment and so-called chromium free techniques are proposed. Among these, some approaches using an organic system compound or organic resin are also proposed, for example, the following approaches can be mentioned.

[0005] (1) The approach using a tannic acid (for example, JP,51-71233,A)

(2) The approach using the thermosetting coating which mixed the tannic acid with an epoxy resin and amino resin (for example, JP,63-90581,A)

(3) How [0006] to use the chelate force of tannic acids, such as an approach (for example, JP,8-

325760,A) using the mixed constituent of drainage system resin and multiple-valued phenolic acid (4)

The surface treatment approach which applies a hydrazine derivative water solution to the front face of a tin plate or a galvanized steel plate (for example, JP,53-27694,B, JP,56-10386,B)

(5) The approach using the rust-proofer containing the amine addition salt which was made to add an amine to the mixture of acyl ZARUKOSHIN and a benzothioria SOL, and was obtained (for example, JP,58-130284,A)

(6) The approach using the processing agent which mixed a heterocyclic compound and tannic acids, such as a benzothiazole compound, (for example, JP,57-198267,A)

[0007]

[Problem(s) to be Solved by the Invention] However, there is a trouble which is described below in these conventional techniques. First, each approach of above-mentioned (1) - (4) has a problem in respect of corrosion resistance. This has a cause in the coat obtained having the self-repair effectiveness by neither of the approaches. That is, with a chromate film, it is (a). The barrier effectiveness: The obstruction effectiveness over corrosion factors (water, oxygen, chlorine, etc.) with a trivalent Cr subject's poorly soluble compound (hydration oxide) (b) The self-repair effectiveness: Discover advanced corrosion resistance according to the synergistic effect of both of the protective film formation effectiveness in the corrosion origin by 6 ** Cr. However, with the conventional chromium free technique, even if not depended on chromium about the barrier effectiveness, organic resin etc. could give to some extent, but about the self-repair effectiveness, since the self-repair nature manifestation matter used as an alternative of 6 ** Cr was not offered, advanced corrosion resistance was unrealizable.

[0008] Moreover, the corrosion resistance of the approach of the above (1) is not only inadequate, but the uniform appearance after processing is not acquired. Moreover, it is not a thing with an eye on especially the approach of the above (2) forming a thin film-like (0.1-5 micrometers) rust-proofing coat in a zinc system or an aluminum system plating front face directly, and even if it applies to a zinc system or an aluminum system plating front face in the shape of a thin film for this reason, sufficient corrosion prevention effectiveness is not acquired. Moreover, corrosion resistance is inadequate similarly about the approach of the above (3).

[0009] The approach of the above (4) is not what was applied about the zinc system or the aluminum system plating steel plate, and even if it applies to a zinc system or an aluminum system plating steel plate, since the coat obtained does not have the network structure, it will not have sufficient barrier nature, and its corrosion resistance will be still more inadequate for this reason. Moreover, although mixing water soluble polymer compounds (polyvinyl alcohol, a maleate copolymer, acrylic ester copolymer, etc.) in a hydrazine derivative water solution with an eye on the homogeneous improvement in a coat is indicated by JP,53-23772,B and JP,56-10386,B, corrosion resistance sufficient with the mere mixture of a hydrazine derivative water solution and a water soluble polymer compound is not acquired.

[0010] Furthermore, the corrosion resistance which was not a thing with an eye on the approach of of the above (5) and (6) also forming a rust-proofing coat in a zinc system or an aluminum system plating steel plate front face for a short time, and was excellent since there was no barrier nature to corrosion factors, such as oxygen and water, even if it applied the processing agent to the plating steel plate front face is not acquired. Moreover, although mixing with resin (an epoxy resin, acrylic resin, urethane resin, nitrocellulose resin, vinyl chloride resin, etc.) is also described as an additive about the approach of (6), corrosion resistance sufficient with the mere mixture of heterocyclic compounds, such as a benzothiazole compound, and resin is not acquired.

[0011] Moreover, in order to remove the oil applied to the front face by press working of sheet metal etc., each approach of above-mentioned (1) - (6) is set on practical use conditions which perform with a pH [by a spray etc.] of about nine to 11 alkaline degreasing, and a coat is exfoliated or damaged with alkaline degreasing, and it has the problem that corrosion resistance cannot be held. Therefore, these approaches are not what was suitable for practical use as an approach of forming a rust-proofing coat.

[0012] Moreover, digitization progresses and, as for the latest OA equipment and the latest AV equipment, severe conductivity has come to be required from a surface treated steel sheet from the cure against a noise. Moreover, spot welding is performed like the assembler of a chassis in many cases, and OA equipment requires the advanced continuation RBI nature in spot welding, in order to secure high productivity. Since the corrosion resistance excellent in the very thin coat is shown in the case of the

organic covering steel plate which has a chromate film, it can respond also to the demand of such severe conductivity or the advanced continuation RBI nature in spot welding, but in the conventional chromium free-lancer's organic covering steel plate, it becomes easy to generate the corrosion from the defective part of a coat, and there is a problem that corrosion resistance falls remarkably by this, so that it becomes a thin film.

[0013] Therefore, the purpose of this invention solves the technical problem of such a conventional technique, and is to offer the organic covering steel plate with which insurance and the corrosion resistance which was harmless and was moreover excellent are acquired excluding heavy metal, such as hexavalent chromium, in a coat also in case it is used, a production process and. Moreover, other purposes of this invention are to offer the organic covering steel plate which has advanced conductivity and spot welding nature with the above outstanding corrosion resistance.

[0014]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of this invention persons' inquiring wholeheartedly, on the front face of a zinc system plating steel plate or an aluminum system plating steel plate While forming a specific multiple oxide coat as the 1st layer coat and forming a specific chelate formation resin coat in the upper part as the 2nd layer coat By carrying out optimum dose combination of the specific self-repair nature manifestation matter (rust-proofing addition component) which replaces hexavalent chromium into this chelate formation resin coat Without performing chromate treatment with a possibility of having a bad influence on an environment or the body, it was pollution-free and found out that the organic covering steel plate which was extremely excellent in corrosion resistance was obtained. Furthermore, it found out that the organic covering steel plate which has advanced conductivity and spot welding nature with the outstanding corrosion resistance was obtained by regulating the coating weight of the 1st layer coat of such an organic covering steel plate, and the 2nd layer coat in the specific range. The configuration by which this invention was made based on such knowledge, and it is characterized [the] is as follows.

[0015] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, [1] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of either of following (a) - (f) is included. (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, Phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, Phosphate and silicon oxide (e) molybdate (f) triazoles The content of the sum total of one or more sorts of organic compound aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[0016] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate, [2] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (g), and (h) is included. (e) The content of the sum total of molybdate (g) calcium, lime compound (h) phosphate, and/or the silicon oxide aforementioned rust-proofing addition component (Y) is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion

resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[0017] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [3] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (e) and the rust-proofing addition component (Y) of (i) are included. The content of the sum total of the (e) molybdate (i) calcium ion-exchange silica aforementioned rust-proofing addition component (Y) is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[0018] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [4] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (f), (g), and (h) is included. (f) triazoles Thiols, thiadiazole, and thiazoles The content of the sum total of one or more sorts of organic compound (g) calcium chosen from thiurams, lime compound (h) phosphate, and/or the silicon oxide aforementioned rust-proofing addition component (Y) receives the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat which is the 1 - 100 weight section (solid content), and whose thickness is 0.1-5 micrometers.

[0019] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [5] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (f) and the rust-proofing addition component (Y) of (i) are included. (f) triazoles The content of the sum total of one or more sorts of (organic compound i) calcium ion-exchange silica aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[0020] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [6] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), Following (e) and the rust-proofing addition component (Y) of (f) are included. (e) molybdate (f) triazoles The content of the sum total of one or more sorts of organic compound aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness

is 0.1-5 micrometers.

[0021] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [7] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (f), (g), and (h) is included. (e) Molybdate (f) triazoles, thiols, and thiadiazole Thiazoles The content of the sum total of one or more sorts of organic compound (g) calcium chosen from thiurams, lime compound (h) phosphate, and/or the silicon oxide aforementioned rust-proofing addition component (Y) receives the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat which is the 1 - 100 weight section (solid content), and whose thickness is 0.1-5 micrometers.

[0022] On the front face of a zinc system plating steel plate or an aluminum system plating steel plate,
 [8] As the 1st layer coat An oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg (gamma), Mn, and aluminum (however, the case where it is contained as a compound and/or a conjugated compound is included), (alpha) It has the multiple oxide coat whose thickness to contain is 0.005-3 micrometers. In the upper part as the 2nd layer coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component (Y) of following (e), (f), and (i) is included. (e) molybdate (f) triazoles The content of the sum total of one or more sorts of (organic compound i) calcium ion-exchange silica aforementioned rust-proofing addition components (Y) chosen from thiols, thiadiazole, thiazoles, and thiurams is the 1 - 100 weight section (solid content) to the said (resultant X) 100 weight section (solid content). The organic covering steel plate excellent in the corrosion resistance characterized by having the organic coat whose thickness is 0.1-5 micrometers.

[0023] [9] The above [1] Organic covering steel plate the organic coat excelled [steel plate] in the corrosion resistance characterized by the content of this solid lubricant (Z) being 1 - 80 weight section (solid content) to the said (resultant X) 100 weight section (solid content) including solid lubricant (Z) further in one organic covering steel plate of - [8].

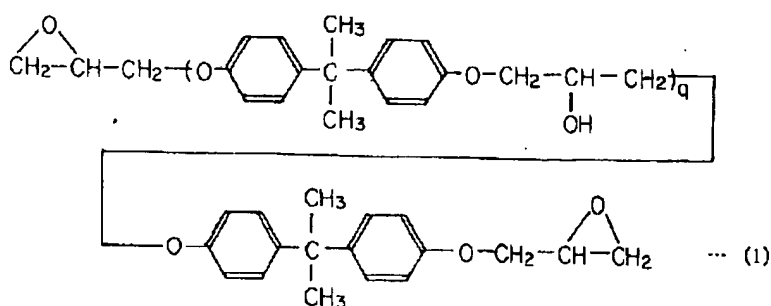
[10] The above [1] Organic covering steel plate which was excellent in the corrosion resistance to which coat formation organic resin (A) is characterized by being epoxy group content resin (D) in one organic covering steel plate of - [9].

[11] The above [1] Organic covering steel plate excellent in the corrosion resistance to which the hydrazine derivative (C) which has active hydrogen is characterized by being the triazole compound which has the pyrazole compound and/or active hydrogen which have active hydrogen in one organic covering steel plate of - [10].

[0024] [12] the hydrazine derivative (C) which has active hydrogen in one organic covering steel plate of above-mentioned [1] - [11] -- the inside of an active hydrogen compound (B) -- 10 - 100-mol % -- the organic covering steel plate excellent in the corrosion resistance characterized by being contained.

[13] The above [10] Organic covering steel plate excellent in the corrosion resistance characterized by being the epoxy resin in which epoxy group content resin (D) is shown by the following formula (1) in one organic covering steel plate of - [12].

[Formula 2]



(q : 0 ~ 50)

[0025] [14] The above [1] Organic covering steel plate excellent in the corrosion resistance characterized by the component (alpha) contained in a multiple oxide coat being silicon oxide in one organic covering steel plate of - [13].

[15] The above [1] Organic covering steel plate excellent in the corrosion resistance characterized by a multiple oxide coat containing organic resin further in one organic covering steel plate of - [14].

[16] The above [1] It is the organic covering steel plate which was excellent in the corrosion resistance to which the sum total coating weight of a component (alpha), the component (beta) in the amount of P2O5 conversions, and the component (gamma) in the amount of metal conversions of Mg, Mn, and aluminum of a multiple oxide coat is 6 - 1000 mg/m², and an organic coat is characterized by coating weight being two or more 0.1 g/m and less than two 0.5 g/m in one organic covering steel plate of - [15].

[0026] [17] The above [1] It is the manufacture approach of one organic covering steel plate of - [16]. On the front face of a zinc system plating steel plate or an aluminum system plating steel plate (b) oxide particle, (**) -- a phosphoric acid and/or a phosphoric-acid compound, and the metal ion of the Mg (Ha), Mn, or the aluminum -- One sort or two sorts or more which are chosen from the groups which consist of the water-soluble ion containing at least one sort in said metal, a compound containing at least one sort in said metal, and a conjugated compound containing at least one sort in said metal, It contains. The mol concentration of said addition component (b), the sum total mol concentration of 2OP5 conversion of said addition component (b), /(Ha) =0.1-20 and the processing liquid adjusted so that a mole ratio (Ha) / (b) =0.1-1.5 might be satisfied are applied. the sum total mol concentration of the amount conversion of metals of said metal of said addition component (Ha) -- mole-ratio (**) -- The multiple oxide coat whose thickness is 0.005-3 micrometers is formed in a plating steel plate front face by carrying out stoving after an appropriate time. Subsequently The manufacture approach of an organic covering steel plate excellent in the corrosion resistance characterized by forming the organic coat whose thickness is 0.1-5 micrometers by applying and carrying out stoving of the coating constituent for organic coat formation to the upper part.

[0027] [18] The manufacture approach of an organic covering steel plate of having excelled in the corrosion resistance characterized by addition component (b) in the processing liquid for multiple oxide coat formation being silicon oxide in the manufacture approach of the above [17].

[19] The manufacture approach of an organic covering steel plate excellent in the corrosion resistance to which the processing liquid for the above-mentioned multiple oxide coat formation is characterized by containing organic resin further in the above [17] or the manufacture approach of [18].

[20] The above [17] In one manufacture approach of - [19] on a plating steel plate front face The sum total coating weight of a component (alpha), the component (beta) in the amount of P2O5 conversions, and the component (gamma) in the amount of metal conversions of Mg, Mn, and aluminum forms the multiple oxide coat of 6 - 1000 mg/m². The manufacture approach of an organic covering steel plate excellent in the corrosion resistance characterized by coating weight forming a two or more 0.1 g/m and less than two 0.5 g/m organic coat in the upper part of this multiple oxide coat.

[0028] The fundamental description of the organic covering steel plate of this invention on the front face of a zinc system plating steel plate or an aluminum system plating steel plate as the 1st layer coat An

oxide particle, a phosphoric acid (beta) and/or a phosphoric-acid compound, and Mg (gamma), (alpha) One or more sorts of metals (however, the case where it is contained as a compound and/or a conjugated compound is included) chosen from Mn and aluminum are contained (preferably). The multiple oxide coat contained as a principal component is formed. In the upper part further as the 2nd layer coat By making the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen react While giving a hydrazine derivative (C) to the resin for coat formation (A) as a chelate formation radical and using the chelate formation resin which is this resultant as base resin As self-repair nature manifestation matter (rust-proofing addition component), (a) calcium ion-exchange silica and phosphate, (b) calcium ion-exchange silica, phosphate and silicon oxide, the (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiadiazole, and thiazoles one or more sorts of organic compounds chosen from thiurams, and ** -- inner either -- or it is in the point in which the organic coat which blended with the above (e) and/or (f) the rust-proofing addition component (Y) which carried out compound addition of other components was formed.

[0029] Although they have the rust-proofing effectiveness which was excellent compared with the conventional chromium free coat also as a respectively independent coat, by this invention, the above-mentioned 1st layer coat and the above-mentioned 2nd layer coat are made into the bilayer coat structure which makes these coats a lower layer and the upper layer, and though it is the coat of a thin film, they make it possible to acquire the corrosion resistance which is equal to a chromate film according to the synergistic effect by this bilayer coat structure. Although the corrosion prevention device by the bilayer coat structure which consists of such a specific multiple oxide coat and a specific organic coat is not necessarily clear, it is thought that it is the result of the corrosion depressant action by both coats that are described below compound-izing.

[0030] although it is not necessarily clear about the corrosion prevention device of the multiple oxide coat which is the above-mentioned 1st layer coat -- ** -- a precise poorly soluble multiple oxide coat intercepts a corrosion factor as barrier sex skin film -- ** Oxide particles, such as silicon oxide, form stable and precise barrier layer anodic oxide coating with a phosphoric acid and/or a phosphoric-acid compound, and one or more sorts of metals chosen from Mg, Mn, and aluminum, ** When an oxide particle is silicon oxide, silicate ion stimulates formation of basic-salt-ized zinc under corrosive environment, and is considered that the anti-corrosiveness which was excellent by raising barrier nature etc. is obtained.

[0031] When a defect furthermore arises in a coat, OH ion generates and an interface becomes alkalinity by the cathode reaction, the above-mentioned component (gamma) precipitates as Me (OH)₂, blocks a defect as a precise poorly soluble product, and is considered to control corrosion reaction. Moreover, as mentioned above, while contributing a phosphoric acid and/or a phosphoric-acid compound to improvement in the compactness of a multiple oxide coat, a phosphoric-acid component catches the zinc ion which dissolved by the anode reaction which is corrosion reaction in a coat defective part, and it is thought that a precipitate product is formed there as a poorly soluble phosphoric-acid zinc compound. As mentioned above, it is thought that a component (gamma), a phosphoric acid, and/or a phosphoric-acid compound show the self-remedial action in a coat defective part.

[0032] Moreover, the corrosion resistance which was excellent also in the above-mentioned component (gamma) especially when a magnesium component was contained is acquired. This is considered that the solubility of Mg of a hydroxide is low compared with other metals, and it is for being easy to form a refractory salt. Moreover, the above operation effectiveness is acquired in SiO₂ particle as a component (alpha) of a multiple oxide coat especially notably [are specific coating weight, and / are specific coating weight about a phosphoric acid and/or a phosphoric-acid compound, and / as a component (gamma) / when it is specific coating weight about a magnesium component and is made to contain, respectively] as a component (beta), as mentioned above.

[0033] Although it is not necessarily clear about the corrosion prevention device of the organic coat which is the above-mentioned 2nd layer coat, the device can be presumed as follows. Namely, by giving a hydrazine derivative to the coat formation organic resin instead of the chelating agent of mere low

molecular weight (1) The effectiveness which intercepts corrosion factors, such as oxygen and a chlorine ion, by the precise organic macromolecule coat is acquired, (2) A hydrazine derivative can be stable, combines with the front face of the 1st layer coat firmly, and can form a passivation layer, (3) In order for the free hydrazine derivative radical in a coat to carry out the trap of the zinc ion eluted by corrosion reaction and to form a stable insoluble chelate compound layer, Advance of corrosion is effectively controlled by the operation effectiveness, like formation of the ionic conduction layer in an interface is controlled, and advance of corrosion is controlled, and it is thought that the outstanding corrosion resistance is acquired.

[0034] Moreover, since precise barrier layer anodic oxide coating is formed of the reaction of epoxy group content resin and a cross linking agent, and this barrier layer anodic oxide coating is excellent in the transparency control ability of corrosion factors, such as oxygen, and the outstanding bonding strength with a base is acquired with the hydroxyl group in a molecule as coat formation organic resin (A) when especially epoxy group content resin is used, the especially excellent corrosion resistance (barrier nature) is acquired. Furthermore, the more excellent corrosion resistance (barrier nature) is acquired by using the triazole compound which has the pyrazole compound and/or active hydrogen which have especially active hydrogen as a hydrazine derivative (C) which has active hydrogen.

[0035] Most improvement effectiveness of corrosion control is not accepted only by mixing a hydrazine derivative to coat formation organic resin like the conventional technique. Although the hydrazine derivative with which the reason is not incorporated into the molecule of coat formation organic resin forms the metal and chelate compound in the 1st layer coat, it is thought that the chelate compound is because it does not become a precise barrier layer for low molecular weight. on the other hand, the corrosion depressor effect which was markedly alike and was excellent is acquired by incorporating a hydrazine derivative into the molecule of coat formation organic resin like this invention.

[0036] In the organic covering steel plate of this invention, moreover, in the organic coat which consists of the above specific resultants (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, Phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, Phosphate and silicon oxide (e) molybdate (f) triazoles Either of one or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams, Or the anti-corrosiveness (the self-repair effectiveness) which was especially excellent in the above (e) and/or (f) by carrying out optimum dose combination of the rust-proofing addition component (Y) which carried out compound addition of other components, and the (self-repair nature manifestation matter) can be obtained. The corrosion prevention device acquired by having blended the component of above-mentioned (a) - (f) into this specific organic coat is considered as follows.

[0037] First, the component of above-mentioned (a) - (d) discovers self-repair nature according to a precipitate operation, and is considered that the reaction mechanism progresses at the following steps.

[The 1st step]: **** calcium carries out the priority dissolution under corrosive environment rather than zinc and aluminum which are a plating metal.

[The 2nd step]: In the case of phosphate, the calcium ion to which the calcium ion which carried out the priority dissolution at the phosphoric-acid ion dissociated by the hydrolysis reaction and the 1st step of the above carried out the priority dissolution of the complexation reaction at the 1st step of the above on the front face in the case of a lifting and silicon oxide adsorbs, and carry out electric neutralization of the surface charge, and condense it. Consequently, in any case, a precise and poorly soluble protective film generates, and corrosion reaction is controlled when this blocks a corrosion origin.

[0038] Moreover, the component of the above (e) discovers self-repair nature according to the passivation effectiveness. That is, a precise oxide is formed in a plating coat front face with dissolved oxygen under corrosive environment, and corrosion reaction is controlled when this blocks a corrosion origin. Moreover, the component of the above (f) discovers self-repair nature according to an adsorption effect. That is, it sticks to the polar group in which the zinc eluted by corrosion and aluminum contain the nitrogen which the component of the above (f) has, and sulfur, and an inactive coat is formed, and corrosion reaction is controlled when this blocks a corrosion origin. Although a certain amount of corrosion prevention effectiveness is acquired even when the component of above-mentioned (a) - (f) is

blended into a general organic coat By having blended the self-repair nature manifestation matter of above-mentioned (a) - (f) into the organic coat excellent in the barrier property which consists of specific chelate modified resin like this invention, both effectiveness (barrier property and self-repair nature) compound-izes, and is considered that the corrosion prevention effectiveness which was extremely excellent by this is demonstrated.

[0039] moreover, considering the self-repair effectiveness acquired by each component of above-mentioned (a) - (d), (e), and (f) For obtaining more advanced self-repair nature, the above (e) and/or (f) are used as an indispensable component. It is desirable to adjust the rust-proofing addition component (Y) of the following combination which compounded other components with this (combination), and the self-repair nature (namely, white-rust-proof) especially, most advanced when it is following (6) and (7) is obtained.

[0040] (1) (e) molybdate, (g) calcium, and/or a lime compound, And rust-proofing addition component which blended (h) phosphate and/or silicon oxide (2) (e) molybdate, And rust-proofing addition component which blended (i) calcium ion-exchange silica (3) (f) triazoles One or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams, (g) Calcium and/or a lime compound and (h) phosphate, and/or silicon oxide, Blended rust-proofing addition component (4) One or more sorts of organic compounds chosen from (f) triazoles, thiols, thiadiazole, thiazoles, and thiurams, and rust-proofing addition component which blended (i) calcium ion-exchange silica [0041] (5) (e) molybdate and (f) triazoles, thiols, One or more sorts of organic compounds chosen from thiadiazole, thiazoles, and thiurams, Blended rust-proofing addition component (6) (e) molybdate and (f) triazoles One or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams, (g) Calcium and/or a lime compound and (h) phosphate, and/or silicon oxide, Blended rust-proofing addition component (7) One or more sorts of organic compounds chosen from (e) molybdate, (f) triazoles, thiols, thiadiazole, thiazoles, and thiurams, and rust-proofing addition component which blended (i) calcium ion-exchange silica [0042] Moreover, since the organic covering steel plate of this invention has advanced corrosion resistance according to a device which was described above, On making it fully decrease and a concrete target, the coating weight of these coats The component (alpha), the component (beta) in the amount of P2O5 conversions, and Mg of the 1st layer coat, The sum total coating weight of the component (gamma) in the amount of metal conversions of Mn and aluminum 6-1000mg, Coating weight of the 2nd layer coat can be made into two or more 0.1 g/m and less than two 0.5 g/m, and it can consider as the organic covering steel plate which has advanced conductivity and spot welding nature with the corrosion resistance which was excellent with this.

[0043]

[Embodiment of the Invention] Hereafter, the detail and its reason for limitation of this invention are explained. As a zinc system plating steel plate used as the base of the organic covering steel plate of this invention A galvanized steel sheet, a Zn-nickel alloy-plating steel plate, a Zn-Fe alloy-plating steel plate (an electroplating steel plate and alloying hot-dip zinc-coated carbon steel sheet), A Zn-Cr alloy-plating steel plate, a Zn-Mn alloy-plating steel plate, a Zn-Co alloy-plating steel plate, A Zn-Co-Cr alloy-plating steel plate, a Zn-Cr-nickel alloy-plating steel plate, A Zn-Cr-Fe alloy-plating steel plate, a Zn-aluminum alloy-plating steel plate For example, (a Zn-5%aluminum alloy-plating steel plate, a Zn-55%aluminum alloy-plating steel plate), A Zn-Mg alloy-plating steel plate, a Zn-aluminum-Mg plating steel plate, the zinc system composite-coatings steel plate (for example, Zn-SiO2 distribution plating steel plate) that distributed the metallic oxide, the polymer, etc. in the plating coat of these plating steel plates can be used further.

[0044] Moreover, the double layer plating steel plate which galvanized congener or a thing of a different kind more than two-layer among the above plating can also be used. Moreover, as an aluminum system plating steel plate used as the base of the organic covering steel plate of this invention, an aluminum plating steel plate, an aluminum-Si alloy-plating steel plate, etc. can be used. Moreover, as a plating steel plate, plating with half-closed eyes, such as nickel, may be beforehand performed to a steel plate side, and the various above plating may be performed on it. As the plating approach, which approach among an electrolytic decomposition process (electrolysis in a water solution or electrolysis in a non-

aqueous solvent), scorification, and gaseous-phase methods which can be enforced is also employable. [0045] Moreover, since it is made for neither a coat defect nor nonuniformity to arise when a bilayer coat which is mentioned later is formed in a plating coat front face, alkaline degreasing, solvent degreasing, surface control processing (alkaline surface control processing, acid surface control processing), etc. can be beforehand processed on a plating coat front face if needed. Moreover, surface control processing by the acidity or the alkaline water solution which contains an iron-group metal ion (nickel ion, Co ion, Fe ion) on a plating coat front face beforehand if needed can also be performed in order to prevent the black discoloration (a kind of the oxidation phenomenon on the front face of plating) under the operating environment of an organic covering steel plate. Moreover, when using an electrolytic zinc-coated carbon steel sheet as a substrate steel plate, an iron-group metal ion (nickel ion, Co ion, Fe ion) can be added to an electroplating bath in order to prevent black discoloration, and 1 ppm or more of these metals can be made to contain in a plating coat. In this case, there is especially no limit about the upper limit of the iron-group metal concentration in a plating coat.

[0046] Next, the multiple oxide coat which is the 1st layer coat formed in the front face of a zinc system plating steel plate or an aluminum system plating steel plate is explained. The alkali silicate processing coats represented by the coat constituent which consists of conventional lithium oxide and silicon oxide completely differ, and this multiple oxide coat is an oxide (alpha) particle (preferably). It is a multiple oxide (it contains as principal component preferably) coat containing silicon oxide, a phosphoric acid (beta) and/or a phosphoric-acid compound, and one or more sorts of metals (however, the case where it is contained as a compound and/or a conjugated compound is included) chosen from Mg (gamma), Mn, and aluminum.

[0047] Especially as an oxide particle which is said component (alpha), silicon oxide (SiO₂ particle) is desirable from a corrosion resistance viewpoint. Moreover, colloidal silica is the most desirable also in silicon oxide. As colloidal silica, for example The Snow tex O by Nissan Chemical Industries, Ltd. The Snow tex OS, the Snow tex OXS, the Snow tex OUP, The Snow tex AK, the Snow tex O40, the Snow tex OL The Snow tex OL 40, the Snow tex OZL, the Snow tex XS, The Snow tex S, the Snow tex NXS, the Snow tex NS, the Snow tex N Snow tex QAS-25 and a catalyst -- formation -- KATAROIDOS made from Industry -- KATAROIDO SI-350, KATAROIDO SI-40, KATAROIDO SA KATAROIDO SN and the Asahi Denka Kogyo K.K. make -- ADERAITO AT-20-50, ADERAITO AT-20N, ADERAITO AT-300, ADERAITO AT-300S, ADERAITOAT20Q, etc. can be used.

[0048] Also in these silicon oxide, especially particle diameter is desirable from a thing 14nm or less and a still more desirable viewpoint of corrosion resistance [thing / 8nm or less]. Moreover, as silicon oxide, the thing which made the coat constituent solution distribute a dry type silica particle can also be used. As this dry type silica, for example, Aerosil 200 made from Japanese Aerosil, Aerosil 3000, Aerosil 300CF, Aerosil 380, etc. can be used, and a thing 7nm or less is still more preferably desirable the particle diameter of 12nm or less especially.

[0049] As an oxide particle, the colloidal solutions, such as an aluminum oxide, a zirconium dioxide, titanium oxide, cerium oxide, and antimony oxide, impalpable powder, etc. can also be used besides the above-mentioned silicon oxide. the coating weight with the viewpoint of corrosion resistance and weldability to the above-mentioned desirable component (alpha) -- 0.01 - 3000 mg/m² -- more -- desirable -- 0.1 - 1000 mg/m² -- it is 1 - 500 mg/m² still more preferably. Moreover, the coating weight with the desirable above-mentioned component (alpha) from a viewpoint of obtaining corrosion resistance, advanced conductivity, and spot welding nature to coincidence is 1 - 600 mg/m².

[0050] The phosphoric acid and/or phosphoric-acid compound which are said component (beta) can be blended as a coat component by adding one sort, such as these metal salts, compounds, etc., such as orthophosphoric acid, a pyrophosphoric acid, polyphosphoric acid, and a metaphosphoric acid, or two sorts or more in a coat constituent. Moreover, one or more sorts of organic phosphorus acids or those salts (for example, phytic acid, a phytic acid salt, phosphonic acid, phosphonate, and these metal salts) may be added to a coat constituent. Moreover, the first phosphate is suitable from the field of the stability of a coat constituent solution also in it.

[0051] Moreover, when one or more sorts of the monobasic ammonium phosphate, dibasic calcium

phosphate, and the third ammonium phosphate were added in the coat constituent solution as phosphate, the inclination for corrosion resistance to be improved more was accepted. Although the reason is not clear, when such ammonium salt is used, even if it makes pH of a coat constituent solution high, liquid does not gel. Generally, in an alkali region, since a metal salt serves as insolubility, when a coat is formed from a coat constituent solution with high pH, it is thought that a more poorly soluble compound arises in a desiccation process.

[0052] There is no limitation also with a special phosphoric-acid [in the inside of a coat] and phosphoric-acid compound's existence gestalt, and it does not ask [a crystal or] whether it is amorphous. Moreover, there is no constraint special also about the phosphoric acid in the inside of a coat, the ionicity of a phosphoric-acid compound, and solubility. the coating weight with viewpoints, such as corrosion resistance and weldability, to the above-mentioned desirable component (beta) -- the amount conversion of P_2O_5 -- 0.01 - 3000 mg/m² -- more -- desirable -- 0.1 - 1000 mg/m² -- it is 1 - 500 mg/m² still more preferably. Moreover, the coating weight with the desirable above-mentioned component (beta) from a viewpoint of obtaining corrosion resistance, advanced conductivity, and spot welding nature to coincidence is 1 - 600 mg/m².

[0053] It is said component (gamma). Especially the gestalt to which one or more sorts of metals chosen from Mg, Mn, and aluminum exist in a coat is not limited, but may exist as a metal as a compound or conjugated compounds, such as an oxide, a hydroxide, a hydration oxide, a phosphoric-acid compound, and a coordination compound. It is not limited about the ionicity of these compounds, a hydroxide, a hydration oxide, a phosphoric-acid compound, a coordination compound, etc., and especially solubility, either.

[0054] Each above-mentioned element which is a component (gamma) forms a phosphoric acid, a phosphoric-acid compound, and an oxide particle and a conjugated compound in a coat, forms the precise barrier sex skin film, and contributes it to corrosion-resistant improvement. Among these elements, OH ion generates by the cathode reaction under corrosive environment, an interface becomes alkalinity, Mg blocks the defect of a coat by precipitating as precise poorly soluble Mg (OH)₂, and it is thought that corrosion reaction is controlled. OH ion generates by the cathode reaction under corrosive environment, an interface becomes alkalinity, and Mn blocks the defect of a coat by precipitating as poorly soluble precise phosphate or a precise poorly soluble hydroxide, and is considered to control corrosion reaction. Moreover, since it is hard to dissolve the phosphate of Mn under an alkali environment when alkaline degreasing washes the processing oil on the front face of a steel plate, slushing oil, volatile oil, etc. by the user, it is very suitable. OH ion generates by the cathode reaction under corrosive environment, an interface becomes alkalinity, and aluminum blocks the defect of a coat by precipitating as precise poorly soluble phosphate, and is considered to control corrosion reaction. Moreover, since it is hard to dissolve the phosphate of aluminum under an alkali environment when alkaline degreasing washes the processing oil on the front face of a steel plate, slushing oil, volatile oil, etc. by the user, it is very suitable.

[0055] What is necessary is just to add to a coat constituent as an approach of introducing a component (gamma) into a coat as the phosphate of Mg, Mn, and aluminum, a sulfate, a nitrate, a chloride, an organic-acid salt, etc. the coating weight with the viewpoint of fall prevention of corrosion resistance and a coat appearance to the above-mentioned desirable component (gamma) -- the amount conversion of metals -- 0.01 - 1000 mg/m² -- more -- desirable -- 0.1 - 500 mg/m² -- there are 1-100mg/[m]² still more preferably. Moreover, the coating weight with the desirable above-mentioned component (gamma) from a viewpoint of obtaining corrosion resistance, advanced conductivity, and spot welding nature to coincidence is 1 - 600 mg/m².

[0056] It is desirable 0.1-20, and that mole-ratio (alpha)/(gamma) (however, a component (gamma) the amount of metal conversions of said metal) of the oxide (alpha) particle which is the constituent of a multiple oxide coat, and one or more sorts of metals (however, the case where it is contained as a compound and/or a conjugated compound is included) chosen from Mg (gamma), Mn, and aluminum sets to 0.1-10 desirably. If this mole-ratio (alpha)/(gamma) is not fully obtained less than by 0.1 but the addition effectiveness of an oxide particle exceeds 20 on the other hand, an oxide particle will check the

eburnation of a coat.

[0057] Moreover, as for mole-ratio (gamma)/(beta) (however, a component (beta) a component (gamma) 2OP5 conversion, the amount conversion of metals of said metal) of the phosphoric acid (beta) and/or phosphoric-acid compound which are the constituent of a multiple oxide coat, and one or more sorts of metals (however, the case where it is contained as a compound and/or a conjugated compound is included) chosen from Mg (gamma), Mn, and aluminum, being referred to as 0.1-1.5 is desirable. Since the poor solubility of a multiple oxide coat is spoiled for this mole ratio with the phosphoric acid of fusibility less than by 0.1 and corrosion resistance falls, it is not desirable. Moreover, since processing liquid ammonia quality will fall remarkably if a mole ratio exceeds 1.5, it is not desirable.

[0058] Into a multiple oxide coat, organic resin can be further blended for the purpose of raising the workability of a coat, and corrosion resistance. As this organic resin, one sort, such as an epoxy resin, urethane resin, acrylic resin, an acrylic-ethylene copolymer, an acrylic-styrene copolymer, alkyd resin, polyester resin, and ethylene resin, or two sorts or more can be used. These can be introduced into a coat as water soluble resin and/or water-dispersion resin. Furthermore, it is effective to use together a water-soluble epoxy resin, water-soluble phenol resin, water-soluble butadiene rubber (SBR, NBR, MBR), melamine resin, block isocyanate, an oxazoline compound, etc. as a cross linking agent in addition to these drainage system resin.

[0059] In a multiple oxide coat, as an additive for raising corrosion resistance further furthermore, a polyphosphate and phosphate (for example, phosphoric-acid zinc and phosphoric-acid 2 hydrogen aluminum --) Molybdate, such as phosphorous acid zinc, molybdophosphate A (molybdophosphoric acid aluminum etc. and organic phosphorus) acid and its salt [for example,] for example, phytic acid, a phytic acid salt, phosphonic acid, phosphonate, and these metal salts -- An alkali-metal salt etc. may blend one sort, such as organic inhibitor (for example, a hydrazine derivative, thiol compounds, dithiocarbamate, etc.) and organic compounds (for example, polyethylene glycol etc.), or two sorts or more.

[0060] furthermore -- as other additives -- an organic color pigment (for example, a condensed multi-ring system organic pigment --) coloring colors (for example, organic solvent fusibility azo dye --), such as a phthalocyanine system organic pigment Inorganic pigments, such as a water-soluble azo metal color (for example, titanium oxide etc.), chelating agents (for example, thiol etc.) and a conductive pigment (for example, zinc --) Metal powder, such as aluminum and nickel, Lynn-ized iron, antimony doping mold tin oxide, etc. can also add one sort, such as coupling agents (for example, a silane coupling agent, a titanium coupling agent, etc.) and a melamine cyanuric acid addition product, or two sorts or more.

[0061] Moreover, in a multiple oxide coat, one or more sorts of an iron-group metal ion (nickel ion, Co ion, Fe ion) may be added in order to prevent the black discoloration (a kind of the oxidation phenomenon on the front face of plating) under the operating environment of an organic covering steel plate. Addition of nickel ion is the most desirable especially. In this case, desired effectiveness will be acquired if there are or more [10000] 1/M as concentration of an iron-group metal ion to component (gamma) 1M (metal conversion) in the amount conversion of metals in a processing constituent. Although especially the upper limit of iron-group ion concentration is not defined, it is desirable to consider as extent which does not affect corrosion resistance with the increment in concentration, and it is desirable 1M and to consider as about 1/100M desirably to component (gamma) 1M (metal conversion).

[0062] The thickness of a multiple oxide coat sets more preferably 0.01-2-micrometer 0.005-3 micrometers [0.1-1-micrometer] to 0.2-0.5 micrometers still more preferably. Corrosion resistance falls [the thickness of a multiple oxide coat] by less than 0.005 micrometers. On the other hand, if thickness exceeds 3 micrometers, conductivity, such as weldability, will fall. moreover, the sum total coating weight which includes the amount of P2O5 conversions of the above-mentioned component (alpha) and the above-mentioned component (beta), and the amount of metal conversions of the above-mentioned component (gamma) when the coating weight prescribes a multiple oxide coat -- 6 - 3600 mg/m2 -- desirable -- 10 - 1000 mg/m2 -- further -- desirable -- 50 - 500 mg/m2 -- it is especially preferably appropriate 100 - 500 mg/m2 and to consider as 200 - 400 mg/m2 most preferably. Corrosion resistance

falls [this sum total coating weight] less than [6mg //m] by two, and on the other hand, if sum total coating weight exceeds 3600 mg/m², since conductivity falls, weldability etc. will fall.

[0063] Moreover, it is appropriate 6 - 1000 mg/m² and to make preferably sum total coating weight of the above (gamma) in the amount of metal conversions of the above-mentioned component (alpha), the above-mentioned component (beta) in the amount of P₂O₅ conversions, and Mg, Mn and aluminum into 10 - 600 mg/m² to obtain advanced conductivity and spot welding nature with corrosion resistance. This sum total coating weight has the insufficient corrosion resistance of less than two 6 mg/m, and on the other hand, if sum total coating weight exceeds 1000 mg/m², the very advanced conductivity and spot welding nature which are considered as a request will not be obtained.

[0064] Next, the organic coat formed in the upper part of the above-mentioned multiple oxide coat as the 2nd layer coat is explained. In this invention, the organic coat formed in the upper part of a multiple oxide coat A resultant with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen (X), The rust-proofing addition component of either of following (a) - (f) which is the self-repair nature manifestation matter (Y), (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, Phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, Phosphate and silicon oxide (e) molybdate (f) triazoles The rust-proofing addition component (Y) which blended other components with one or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams or the above (e), and/or (f) is included. Furthermore, the thickness with which solid lubricant (Z) was blended if needed is the organic coat which is 0.1-5 micrometers.

[0065] If it is resin which it can react with the active hydrogen content compound (B) with which a part or all compounds consist of a hydrazine derivative (C) which has active hydrogen as a class of coat formation organic resin (A), and an active hydrogen content compound (B) can combine with coat formation organic resin by reactions, such as addition and condensation, and can form a coat appropriately, there will be no special constraint. As this coat formation organic resin (A), an addition product or a condensate of an epoxy resin, a modified epoxy resin, polyurethane resin, polyester resin, alkyd resin, the acrylic copolymer resin, a polybutadiene resin, phenol resin, and these resin etc. can be mentioned, it is independent in one of sorts of these, or two or more sorts can be mixed and used, for example.

[0066] Moreover, as coat formation organic resin (A), the epoxy group content resin (D) which contains an epoxy group in resin from points, such as reactivity, an ease of a reaction, and anti-corrosiveness, is especially desirable. It reacts with the active hydrogen content compound (B) with which a part or all compounds consist of a hydrazine derivative (C) which has active hydrogen as this epoxy group content resin (D). An active hydrogen content compound (B) can combine with coat formation organic resin by reactions, such as addition and condensation. And if it is resin which can form a coat appropriately, there will be no special constraint. For example, an epoxy resin, a modified epoxy resin, an epoxy group content monomer and copolymerized acrylic copolymer resin, An addition product or a condensate of the polybutadiene resin which has an epoxy group, the polyurethane resin which has an epoxy group, and these resin etc. can be mentioned, it is independent, or two or more sorts can be mixed and one sort of these epoxy group content resin can be used.

[0067] Moreover, an epoxy resin and especially a modified epoxy resin are suitable from the adhesion on the front face of plating, and a corrosion resistance point also in these epoxy group content resin (D). Moreover, also in it, the thermosetting epoxy resin and thermosetting modified epoxy resin which have the cutoff nature which was excellent to corrosion factors, such as oxygen, are the optimal, and it is advantageous especially when making coating weight of a coat into a low, in order to obtain especially advanced conductivity and spot welding nature.

[0068] Make polyphenol, such as bisphenol A, Bisphenol F, and a novolak mold phenol, and epihalohydrin, such as epichlorohydrin, react, and come to introduce a glycidyl group, or polyphenol is made to react to this glycidyl group installation resultant further as the above-mentioned epoxy resin, an aliphatic series epoxy resin, an alicycle group epoxy resin, etc. are mentioned to the aromatic series epoxy resin and pan which make molecular weight come to increase, it is independent about these one

sort, or two or more sorts can be mixed and used. When it needs film-forming [in low temperature], it is suitable for especially these epoxy resins that number average molecular weight is 1500 or more.

[0069] The epoxy acrylate resin which denaturalized of the polymerization nature partial saturation monomer component containing epoxy ester resin, an acrylic acid, or a methacrylic acid etc. to which could mention the resin which made various modifiers react to the epoxy group or hydroxyl group in the above-mentioned epoxy resin as the above-mentioned modified epoxy resin, for example, the drying-oil fatty acid was made to react, the urethane modified epoxy resin to which the isocyanate compound was made to react can be illustrated.

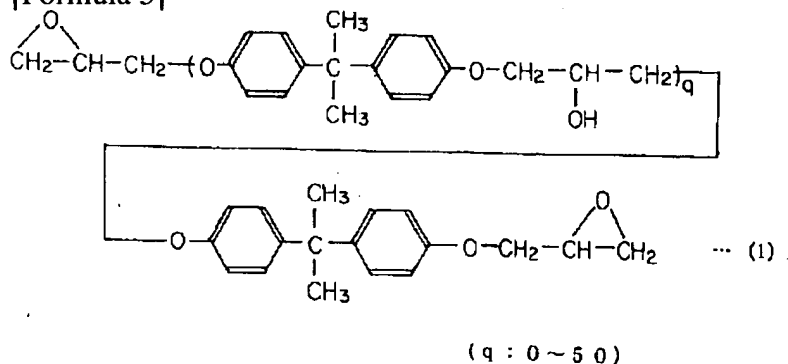
[0070] The resin which compounded the polymerization nature partial saturation monomer component which makes indispensable the above-mentioned epoxy group content monomer, the partial saturation monomer which has an epoxy group as copolymerized acrylic copolymer resin, acrylic ester, or methacrylic ester by the solution polymerization method, the emulsion polymerization method, or the suspension-polymerization method can be mentioned.

[0071] As the above-mentioned polymerization nature partial saturation monomer component, for example Methyl (meta) acrylate, Ethyl (meta) acrylate, propyl (meta) acrylate, n-, iso-, or tert-butyl (meta) acrylate, Hexyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, C1 - 24 alkyl ester of acrylic acids, such as DESHIRU (meta) acrylate and lauryl (meta) acrylate, or a methacrylic acid; An acrylic acid, A methacrylic acid, styrene, vinyltoluene, acrylamide, acrylonitrile, C1 - 4 alkyl-ether ghost;N of N-methylol(metha)acrylamide and N-methylol(metha)acrylamide, N-diethylamino ethyl methacrylate, etc. can be mentioned.

[0072] Moreover, as a partial saturation monomer which has an epoxy group, if glycidyl methacrylate, glycidyl acrylate, 3, and 4-epoxycyclohexylmethyl (meta) acrylate etc. has an epoxy group and a polymerization nature partial saturation radical, there will be no special constraint. Moreover, this epoxy group content monomer and the copolymerized acrylic copolymer resin can also be used as the resin denatured with polyester resin, an epoxy resin, phenol resin, etc.

[0073] Especially a desirable thing is resin which has the chemical structure shown in following the (1) type which is the resultant of bisphenol A and epihalohydrin as said epoxy resin, and since especially this epoxy resin is excellent in corrosion resistance, it is desirable.

[Formula 3]



The manufacturing method of such a bisphenol A mold epoxy resin is widely known in this industry. moreover, the above-mentioned chemical structure type -- setting -- q -- 0-50 -- desirable -- 1-40 -- it is 2-20 especially preferably. In addition, coat formation organic resin (A) may be organic solvent dissolution mold, organic solvent distributed-process-input-output-equipment, aqueous solution type, and moisture powder type any.

[0074] At this invention, it aims at giving a hydrazine derivative into the molecule of coat formation organic resin (A), and, for this reason, some active hydrogen content compounds [at least] (B) (preferably all) need to be the hydrazine derivative (C) which has active hydrogen.

[0075] Although a thing as shown below as that epoxy group and an active hydrogen content compound (B) which reacts can be illustrated and these one sort or two sorts or more can be used when coat formation organic resin (A) is epoxy group content resin, it is required to be the hydrazine derivative

with which some active hydrogen content compounds [at least] (B) (preferably all) have active hydrogen also in this case.

- The 4th class chlorination agent which is the mixture of the hydrazine derivative or tertiary amine which does not have hydrogen halide and alcohols, such as an organic acid, hydrogen chlorides, etc., such as an amine compound and ammonia of the 1st class which has the hydrazine derivative and active hydrogen which has active hydrogen, or the 2nd class, and a carboxylic acid, and thiols and active hydrogen, and an acid [0076] As a hydrazine derivative (C) which has said active hydrogen, the following can be mentioned, for example.

** Hydrazide compounds, such as KARUBO hydrazide, propionic-acid hydrazide, salicylic-acid hydrazide, adipic-acid dihydrazide, sebacic-acid dihydrazide, dodecanoic acid dihydrazide, isophthalic acid dihydrazide, thio KARUBO hydrazide, 4, and 4'-oxybis benzene sulfonylhydrazide, a benzophenone hydrazone, and amino polyacrylamide;

** Pyrazole compounds, such as a pyrazole, 3, 5-dimethylpyrazol, a 3-methyl-5-pyrazolone, and 3-amino-5-methyl pyrazole;

[0077] ** 1, 2, 4-triazole, 3-amino-1,2,4-triazole, 4-amino - 1, 2, 4-triazole, 3-mercapto - 1, 2, 4-triazole, 5-amino-3-mercapto - 1, 2, 4-triazole, 2, 3-dihydro-3-oxo-- 1, 2, 4-triazole, 1H-benzotriazol, 1-hydroxy benzotriazol (one hydrate), 6-methyl-8-hydroxy triazolo pyridazine, 6-phenyl-8-hydroxy triazolo pyridazine, 5-hydroxy-7-methyl - Triazole compounds, such as 1, 3, and 8-TORIAZA indolizine;

[0078] ** 5-phenyl - 1, 2, 3, 4-tetrazole, 5-mercapto-1-phenyl - Tetrazole compounds, such as 1, 2, 3, and 4-tetrazole;

** 5-amino-2-mercapto - Thiadiazole compounds, such as 1, 3, 4-thiadiazole, and 2,5-dimercapto-1,3,4-thiadiazole;

** Pyridazine compounds, such as maleic hydrazide, 6-methyl-3-pyridazone, 4, 5-dichloro-3-pyridazone, 4, 5-dibromo-3-pyridazone, the 6-methyl -4, and 5-dihydro-3-pyridazone [0079] Moreover, especially the pyrazole compound and triazole compound that have the cyclic structure of a five-membered ring or six membered-rings, and have a nitrogen atom in cyclic structure also in these are suitable. These hydrazine derivatives are independent in one sort, or can mix and use two or more sorts. [0080] As an example of representation of the amine compound which has the above-mentioned active hydrogen which can be used as some active hydrogen content compounds (B), the following can be mentioned, for example.

** Compound which was made to carry out the pyrogenetic reaction of the 1st class amino group of the amine compound containing the one 2nd class amino groups, such as diethylenetriamine, hydroxyethylamino ethylamine, ethylamino ethylamine, and methylamino propylamine, and the one or more 1st class amino groups to a ketone, an aldehyde, or a carboxylic acid at the temperature of about 100-230 degrees C, and denaturalized to aldimine, ketimine, oxazoline, or imidazoline;

[0081] ** The 2nd class monoamines, such as diethylamine, diethanolamine, and G n- or -iso-propanolamine, N-methylethanol amine, and N-ethyl ethanolamine;

** Secondary amine content compound which was made to add mono-alkanolamine like monoethanolamine, and dialkyl (meta) acrylamide by the Michael addition reaction, and was obtained;

** Compound which denaturalized the 1st class amino group of alkanolamines, such as monoethanolamine, a neo pentanol amine, 2-amino propanol, 3-amino propanol, and 2-hydroxy-2' (amino propoxy) ethyl ether, to ketimine;

[0082] Since the hydrazine derivative or tertiary amine in which the above-mentioned 4th class chlorination agent which can be used as some active hydrogen content compounds (B) does not have active hydrogen does not have an epoxy group and reactivity in itself, in order to enable an epoxy group and the reaction of these, it is taken as mixture with an acid. The 4th class chlorination agent reacts with an epoxy group under existence of water if needed, and forms epoxy group content resin and the 4th class salt.

[0083] Any of inorganic acids, such as organic acids, such as an acetic acid and a lactic acid, and a hydrochloric acid, are sufficient as the acid used in order to obtain the 4th class chlorination agent. Moreover, 3,6-dichloro pyridazine etc. can be mentioned as a hydrazine derivative which does not have

active hydrogen used in order to obtain the 4th class chlorination agent, and dimethylethanolamine, triethylamine, a trimethylamine, a triisopropyl amine, methyldiethanolamine, etc. can be mentioned as tertiary amine, for example.

[0084] The resultant (X) with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen makes coat formation organic resin (A) and 10-300 degrees C (B) of active hydrogen content compounds react at 50-150 degrees C preferably for about 1 to 8 hours, and is acquired.

[0085] This reaction may be performed by adding an organic solvent, and especially the class of organic solvent to be used is not limited. For example, an acetone, a methyl ethyl ketone, methyl isobutyl ketone, Ketones, such as a dibutyl ketone and a cyclohexanone; Ethanol, a butanol, 2-ethylhexyl alcohol, benzyl alcohol, ethylene glycol, Ethylene glycol mono-isopropyl ether, ethylene glycol monobutyl ether, The ethylene glycol mono-hexyl ether, propylene glycol, Propylene glycol monomethyl ether, a diethylene glycol, Alcohols and ether containing hydroxyl groups, such as diethylene glycol monoethyl ether and the diethylene-glycol monobutyl ether; Ethyl acetate, Ester, such as butyl acetate and ethylene-glycol-monobutyl-ether acetate; aromatic hydrocarbon, such as toluene and a xylene, etc. can be illustrated and these one sort or two sorts or more can be used. Moreover, from fields, such as solubility with an epoxy resin, and a paint film plasticity, especially the solvent of a ketone system or an ether system is desirable in these.

[0086] As for the rate of a compounding ratio with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen, it is desirable at a rate of solid content 0.5 - 20 weight section and to make an active hydrogen content compound (B) into 1.0 - 10 weight section preferably especially to the coat formation organic (resin A) 100 weight section.

[0087] moreover, when coat formation organic resin (A) is epoxy group content resin (D) The rate of a compounding ratio of epoxy group content resin (D) and an active hydrogen content compound (B) the ratio [active hydrogen of the number of the active hydrogen radicals of an active hydrogen content compound (B), and the number of the epoxy groups of epoxy group content resin (D) -- the base -- number of /epoxy groups] -- 0.01-10 -- it is more preferably appropriate from points, such as corrosion resistance, 0.1-8, and to be referred to as 0.2-4 still more preferably.

[0088] moreover, the rate of a hydrazine derivative (C) of having active hydrogen in an active hydrogen content compound (B) -- 10 - 100-mol % -- more -- desirable -- 30 - 100-mol % and a pan -- it is appropriate to consider as 40 - 100-mol % preferably. The rate of a hydrazine derivative (C) of having active hydrogen cannot give rust-proofing function sufficient less than [10 mol %] for an organic coat, but the rust-proofing effectiveness acquired becomes practically equal with the case where coat formation organic resin and a hydrazine derivative are used having only mixed.

[0089] In order to form precise barrier layer anodic oxide coating in this invention, it is desirable to blend a curing agent into a resin constituent and to carry out heat hardening of the organic coat. As the hardening approach in the case of forming a resin constituent coat (1) The hardening approach of using the urethane-ized reaction of isocyanate and the hydroxyl group in base resin, (2) Melamine, The etherification reaction between the hydroxyl groups in the alkyl ether-ized amino resin which makes the monohydric alcohol of carbon numbers 1-5 come to react to some or all of a methylol compound that makes formaldehyde come to react to one or more sorts chosen from a urea and benzoguanamine, and base resin Although hardening approach ** to be used is suitable, especially the thing for which the urethane-ized reaction of isocyanate and the hydroxyl group in base resin is made into a main reaction is suitable.

[0090] The poly isocyanate compound used by the hardening approach of the above (1) is a compound which carried out the partial reaction of the aliphatic series and the alicycle group (heterocycle is included) who have at least two isocyanate radicals in 1 molecule, aromatic series isocyanate compounds, or those compounds with polyhydric alcohol. As such a poly isocyanate compound, the following can be illustrated, for example.

** m- or p-phenylene diisocyanate, 2, and 4- or 2, 6-tolylene diisocyanate, o- or p-xylylene diisocyanate,

hexamethylene di-isocyanate, dimer acid diisocyanate, isophorone diisocyanate [0091] ** the compound of the above-mentioned ** -- independent or the compound with which it is the resultant of those mixture and polyhydric alcohol (tetravalent alcohol [, such as trihydric alcohol; pentaerythritol], such as dihydric alcohol; glycerols, such as ethylene glycol and propylene glycol, and trimethylol propane; 6 ** alcohol, such as a sorbitol and dipentaerythritol etc.), and at least two isocyanates remain in 1 molecule - the poly isocyanate compound of these is independent about one sort, or two or more sorts can be mixed and used for it.

[0092] moreover, as a protective agent (block agent) of the poly isocyanate compound For example, ** methanol, ethanol, propanol, a butanol, The mono-ether of aliphatic series monoalcohol ** ethylene glycol, such as octyl alcohol, and/or a diethylene glycol, For example, mono-ether ** phenols, such as methyl, ethyl, propyl (n-, -, iso), and butyl (n-, iso, sec), By being able to use oximes, such as aromatic alcohol ** aceto oximes, such as cresol, and methyl ethyl ketone oxime, etc., and making these one sort or two sorts or more, and said poly isocyanate compounds react The poly isocyanate compound protected by stability under ordinary temperature at least can be obtained.

[0093] It is appropriate (A)/(E) = 95 / 5 - 55/45 (weight ratio of a nonvolatile matter), and to blend such a poly isocyanate compound (E) preferably to coat formation organic resin (A) at a rate of (A)/(E) = 90 / 10 - 65/35 as a curing agent. There is absorptivity in the poly isocyanate compound, and if this is blended exceeding (A)/(E) = 55/45, the adhesion of an organic coat will be degraded. Furthermore, when finishing paint is performed on an organic coat, the unreacted poly isocyanate compound will move into a paint film, and it will cause hardening inhibition and poor adhesion of a paint film. As for the loadings of such a viewpoint to the poly isocyanate compound (E), it is desirable to carry out to or less (A)/(E) = 55/45.

[0094] In addition, although coat formation organic resin (A) fully constructs a bridge by addition of the above cross linking agents (curing agent), in order to increase low-temperature cross-linking further, it is desirable to use a well-known hardening accelerator catalyst. As this hardening accelerator catalyst, N-ethyl morpholine, a dibutyl tin JIRAU rate, naphthenic-acid cobalt, the 1st tin of chlorination, zinc naphthenate, a bismuth nitrate, etc. can be used, for example. Moreover, when using epoxy group content resin, for example for coat formation organic resin (A), resin, such as a well-known acrylic, alkyd, and polyester, can also be mixed and used with epoxy group content resin with an eye on some improvement in physical properties, such as adhesion.

[0095] The rust-proofing addition component of either of following (a) - (f) which is the self-repair nature manifestation matter in an organic coat in this invention (Y), (a) calcium ion-exchange silica and a phosphate (b) calcium ion-exchange silica, Phosphate, a silicon oxide (c) lime compound, and a silicon oxide (d) lime compound, The rust-proofing addition component (Y) which blended other components with one or more sorts of organic compounds chosen from phosphate and silicon oxide (e) molybdate (f) triazoles, thiols, thiadiazole, thiazoles, and thiurams or the above (e), and/or (f) is added. These components (a) It is as having described the corrosion prevention device by - (f) previously.

[0096] The above-mentioned component (a) and calcium ion-exchange silica contained in (b) are what fixed calcium ion to the front face of porosity silica gel powder, and calcium ion is emitted under corrosive environment and it forms precipitation membrane. Although the thing of arbitration can be used as a calcium ion-exchange silica, the thing 4 micrometers or less of mean particle diameter is desirably desirable, for example, it can use 6 micrometers or less of things whose mean particle diameter is 2-4 micrometers. If the mean particle diameter of calcium ion-exchange silica exceeds 6 micrometers, while corrosion resistance will fall, the distributed stability in the inside of a coating constituent falls.

[0097] As for calcium concentration in calcium ion-exchange silica, it is desirable more than 1wt% and that it is 2 - 8wt% desirably. Less than [1wt%], the rust-proofing effectiveness according [calcium concentration] to calcium emission is not fully acquired. In addition, it is not limited about the surface area of calcium ion-exchange silica, pH, and especially oil absorption.

[0098] As above calcium ion-exchange silicas It is SHIELDEX C303 (the mean particle diameter of 2.5-3.5 micrometers) made from W.R.Grace&Co. at a trade name. calcium concentration 3wt%, SHIELDEX AC3 (the mean particle diameter of 2.3-3.1 micrometers) calcium concentration 6wt%,

SHIELDEX AC5 (the mean particle diameter of 3.8-5.2 micrometers) SHIELDEX made from Fuji SHIRISHIA Chemistry (mean-particle-diameter [of 3 micrometers], calcium concentration 6 - 8wt%), SHIELDEX SY710 (mean-particle-diameter [of 2.2-2.5 micrometers], calcium concentration 6.6 - 7.5wt%), etc. can be used calcium concentration 6wt%.

[0099] The phosphate contained in the above-mentioned component (a), (b), and (d) contains the salt of all classes, such as simple salt and double salt. Moreover, limitation may not be in the metal cation which constitutes it, and which metal cations, such as phosphoric-acid zinc, magnesium phosphate, calcium phosphate, and aluminium phosphate, are sufficient. Moreover, there is no limitation in whenever [frame / of phosphoric-acid ion /, or condensation] etc., any of normal salt, 2 hydrogen salt, 1 hydrogen salt, or phosphite are sufficient, and normal salt contains all condensed phosphates, such as a polyphosphate besides an orthophosphate, further.

[0100] Any of a calcium oxide, a calcium hydroxide, and a calcium salt are sufficient as the above-mentioned component (c) and the lime compound contained in (d), and these one sort or two sorts or more can be used for it. Moreover, a peach is good using the double salt containing cations other than calcium, such as calcium phosphate and zinc besides the simple salt which especially a limit does not have in the class of calcium salt, either, and contains only calcium as cations, such as a calcium silicate, a calcium carbonate, and calcium phosphate, and calcium phosphate magnesium, and calcium.

[0101] Any of colloidal silica and a dry type silica are sufficient as the silicon oxide contained in the above-mentioned component (b), (c), and (d). As colloidal silica, in using drainage system coat formation resin as the base By the trade name, for example, the Snow tex O by Nissan Chemical Industries, Ltd., Snow tex N The Snow tex 20, the Snow tex 30, the Snow tex 40, the Snow tex C the Snow tex S and a catalyst -- formation -- Industry -- KATAROIDOS of make, KATAROIDO SI-350, KATAROIDO SI-40, and KATAROIDO SA -- KATAROIDO SN, ADERAITO AT-20-50 by Asahi Denka Kogyo K.K., ADERAITO AT-20N, ADERAITO AT-300, ADERAITO AT-300S, ADERAITOAT20Q, etc. can be used.

[0102] moreover, in using solvent system coat formation resin as the base By the trade name, for example, ORGANO silica sol MA-ST-M by Nissan Chemical Industries, Ltd., ORGANO silica sol IPA-ST, ORGANO silica sol EG-ST, ORGANO silica sol E-ST-ZL, ORGANO silica sol NPC-ST, ORGANO silica sol DMAC-ST, ORGANO silica sol DMAC-ST-ZL, ORGANO silica sol XBA-ST, ORGANO silica sol MIBK-ST, a catalyst -- formation -- Industry -- OSCAL-1132 of make, OSCAL-1232, and OSCAL- 1332, OSCAL-1432, OSCAL-1532, OSCAL-1632, OSCAL-1722, etc. can be used.

[0103] Especially an organic solvent distributed silica sol is excellent in dispersibility, and excels fumed silica in corrosion resistance. Moreover, as fumed silica, AEROSIL R971, AEROSIL R812, AEROSIL R811, AEROSIL R974, AEROSIL R202, AEROSILR805 and AEROSIL130 made from Japanese Aerosil, AEROSIL 200, AEROSIL300, AEROSIL 300CF, etc. can be used by the trade name, for example.

[0104] It is thought that a particle silica can control promotion of corrosion by contributing to generation of the corrosion product of precise and stable zinc under corrosive environment, and forming this corrosion product in a plating front face precisely. As for a particle silica, from a corrosion resistance viewpoint, it is desirable that particle diameter uses desirably 5-50nm of 5-20nm of 5-15nm things still more preferably.

[0105] Limitation does not have molybdate of said component (e) in whenever [frame and condensation], for example, alt.molybdate, paramolybdate, metamolybdate, etc. are mentioned. Moreover, as double salt, phosphoric-acid molybdate etc. is mentioned including all salts, such as simple salt and double salt.

[0106] As triazoles, among the organic compounds of the above-mentioned component (f) 1, 2, 4-triazole, 3-amino-1,2,4-triazole, 3-mercapto - 1, 2, 4-triazole, 5-amino-3-mercapto - 1, 2, 4-triazole, 1H-benzotriazol, etc. again as thiols 1,3,5-triazine-2,4,6-trithiol, 2-mercapto Benz imidazole, etc. again as thiadiazole 5-amino-2-mercapto - 1, 3, 4-thiadiazole, 2,5-dimercapto-1,3,4-thiadiazole, etc. again as thiazoles 2-N and N-diethylthio benzothiazole and 2-mercaptobenzothiazole are mentioned for a tetraethylthiuram disulfide etc. as thiurams again, respectively.

[0107] the above-mentioned component (a) -- setting -- the compounding ratio of calcium ion-exchange silica (a1) and phosphate (a2) -- the weight ratio of solid content -- $(a1) / (a2) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. Less than by $1/99$, $(a1)/(a2)$ has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin. On the other hand, if $99/1$ is exceeded, since phosphoric-acid ion required for formation of a protective film to start the calcium and complexation reaction for the calcium of the amount beyond the need to not only be eluted, but will not be supplied enough, corrosion resistance will fall on the contrary.

[0108] In the above-mentioned component (b) $20 / 80 - 80/20$ are still more preferably suitable. the compounding ratio of calcium ion-exchange silica (b1), phosphate (b2), and silicon oxide (b3) -- the weight ratio of solid content -- $(b1) / (b2) + (b3) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. [moreover (b2),] Less than $(b2) 1/99$ and $(b3)$ have few calcium elution volumes and amounts of phosphoric-acid ion less than $1/99$, and $(b1) / (b2) + (b3)$ cannot form only the protective film which blocks a corrosion origin. When $(b1) / (b2) + (b3)$ exceeds $99/1$, on the other hand, the calcium of the amount beyond the need is not only eluted for formation of a protective film, but Silicon oxide required for making phosphoric-acid ion and calcium required starting the calcium and complexation reaction adsorb is not fully supplied. Moreover, silicon oxide required for making the calcium eluted when $(b2)/(b3)$ exceeded $99/1$ adsorb is not fully supplied, but also when it is any, corrosion resistance will fall on the contrary.

[0109] the above-mentioned component (c) -- setting -- the compounding ratio of a lime compound (c1) and silicon oxide (c2) -- the weight ratio of solid content -- $(c1) / (c2) = 1 - 99 - 99 / 1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. Less than by $1/99$, $(c1)/(c2)$ has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin. On the other hand, if $99/1$ is exceeded, since silicon oxide required for making the calcium the calcium of the amount beyond the need not only being to elute, but adsorb for formation of a protective film will not fully be supplied, corrosion resistance will fall on the contrary.

[0110] In the above-mentioned component (d) $20 / 80 - 80/20$ are still more preferably suitable. the compounding ratio of a lime compound (d1), phosphate (d2), and silicon oxide (d3) -- the weight ratio of solid content -- $(d1) / (d2) + (d3) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $(d2) / (d3) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. Less than $(d2) 1/99$ and $(d3)$ have few calcium elution volumes and amounts of phosphoric-acid ion less than $1/99$, and $(d1) / (d2) + (d3)$ cannot form only the protective film which blocks a corrosion origin. When $(d1) / (d2) + (d3)$ exceeds $99/1$, on the other hand, the calcium of the amount beyond the need is not only eluted for formation of a protective film, but Silicon oxide required for making phosphoric-acid ion and calcium required starting the calcium and complexation reaction adsorb is not fully supplied. Moreover, silicon oxide required for making the calcium eluted when $(d2)/(d3)$ exceeded $99/1$ adsorb is not fully supplied, but also when it is any, corrosion resistance will fall on the contrary.

[0111] Above-mentioned rust-proofing addition component (a) - (f) forms a protective film in the bottom of corrosive environment, respectively according to the precipitate effectiveness (component (a) in the case of - (d)), the passivation effectiveness (in the case of a component (e)), and an adsorption effect (in the case of a component (f)), as stated previously. The corrosion prevention effectiveness which was extremely excellent in the specific chelate formation resin which is especially base resin in this invention when the self-repair effectiveness by the barrier effectiveness by chelate formation resin and above-mentioned (component a) above-mentioned component (a) - (f) compound-ized by blending either of - (f) is demonstrated.

[0112] moreover, considering the self-repair effectiveness (the protective film formation effectiveness of three types mentioned above) acquired by each component of above-mentioned (a) - (d), (e), and (f) It is desirable to adjust the rust-proofing addition component (Y) of the following combination which carried out compound addition of other components in obtaining more advanced self-repair nature at the above (e) and/or (f) (combination), and the self-repair nature (namely, white-rust-proof) especially, most advanced when it is following (6) and (7) is obtained.

(1) Rust-proofing addition component which blended (e) molybdate, (g) calcium and/or a lime

compound and (h) phosphate, and/or silicon oxide (2) (e) molybdate and rust-proofing addition component which blended (i) calcium ion-exchange silica [0113] (3) (f) triazoles, thiols, thiadiazole, and thiazoles One or more sorts of the organic compounds, (g) calcium, and/or the lime compounds which are chosen from thiurams, And rust-proofing addition component which blended (h) phosphate and/or silicon oxide (4) (f) triazoles One or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams, And rust-proofing addition component which blended (i) calcium ion-exchange silica (5) Rust-proofing addition component which blended one or more sorts of organic compounds chosen from (e) molybdate and (f) triazoles, thiols, thiadiazole, thiazoles, and thiurams [0114] (6) (e) molybdate, (f) triazoles, thiols, One or more sorts of organic compounds chosen from thiadiazole, thiazoles, and thiurams, (g) Calcium and/or a lime compound and (h) phosphate, and/or silicon oxide, Blended rust-proofing addition component (7) (e) molybdate and (f) triazoles one or more sorts of organic compounds chosen from thiols, thiadiazole, thiazoles, and thiurams, and the rust-proofing addition component which blended (i) calcium ion-exchange silica -- here About the lime compound which can be applied, phosphate, silicon oxide, and calcium ion-exchange silica, it is the same as that of what was previously described about the component of (a) - (d).

[0115] In the rust-proofing addition component which blended (e) molybdate, (g) calcium and/or the lime compound and (h) phosphate, and/or silicon oxide of the above (1) 20 / 80 - 80/20 are still more preferably suitable. the compounding ratio of these (e), (g), and (h) -- the weight ratio of solid content -- $(e)/(g)+(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $(g)/(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- 20 / 80 - 80/20 are still more preferably suitable. [moreover,]

[0116] Here, the effectiveness by $(e)/(g)+(h)$ compounding less than 1/99 and then different self-repair effectiveness by exceeding 99/1 is not fully acquired. Moreover, if $(g)/(h)$ has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin less than by 1/99 but 99/1 is exceeded on the other hand Since silicon oxide required for making phosphoric-acid ion and calcium required starting the calcium and complexation reaction the calcium of the amount beyond the need not only being eluted, but adsorb for formation of a protective film is not fully supplied, sufficient self-repair effectiveness is not acquired.

[0117] the rust-proofing addition component which blended (e) molybdate of the above (2), and (i) calcium ion-exchange silica -- setting -- the compounding ratio of (e) and (i) -- the weight ratio of solid content -- $(e)/(i) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- 20 / 80 - 80/20 are still more preferably suitable. Here, the effectiveness by $(e)/(i)$ compounding less than 1/99 and then different self-repair effectiveness by exceeding 99/1 is not fully acquired.

[0118] (f) triazoles of the above (3), thiols, and thiadiazole In the rust-proofing addition component which blended one or more sorts chosen from thiazoles and thiurams of an organic compound, (g) calcium and/or lime compounds and (h) phosphate, and/or silicon oxide 20 / 80 - 80/20 are still more preferably suitable. the compounding ratio of these (f), (g), and (h) -- the weight ratio of solid content -- $(f)/(g)+(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $(g)/(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- 20 / 80 - 80/20 are still more preferably suitable. [moreover,]

[0119] Here, the effectiveness by $(f)/(g)+(h)$ compounding less than 1/99 and then different self-repair effectiveness by exceeding 99/1 is not fully acquired. Moreover, if $(g)/(h)$ has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin less than by 1/99 but 99/1 is exceeded on the other hand Since silicon oxide required for making phosphoric-acid ion and calcium required starting the calcium and complexation reaction the calcium of the amount beyond the need not only being eluted, but adsorb for formation of a protective film is not fully supplied, sufficient self-repair effectiveness is not acquired.

[0120] In the rust-proofing addition component which blended one or more sorts of organic compounds chosen from (f) triazoles of the above (4), thiols, thiadiazole, thiazoles, and thiurams, and (i) calcium ion-exchange silica (f) -- and the compounding ratio of (i) -- the weight ratio of solid content -- $(f)/(i) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- 20 / 80 - 80/20 are still more preferably suitable. Here, the effectiveness by $(f)/(i)$ compounding less than 1/99 and then different self-repair effectiveness by exceeding 99/1 is not fully acquired.

[0121] In the rust-proofing addition component which blended one or more sorts of organic compounds chosen from (e) molybdate of the above (5) and (f) triazoles, thiols, thiadiazole, thiazoles, and thiurams (e) -- and the compounding ratio of (f) -- the weight ratio of solid content -- $(e)/(f) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. Here, the effectiveness by (e)/(f) compounding less than $1/99$ and then different self-repair effectiveness by exceeding $99/1$ is not fully acquired.

[0122] (e) molybdate of the above (6), (f) triazoles, thiols, In the rust-proofing addition component which blended one or more sorts chosen from thiadiazole, thiazoles, and thiurams of an organic compound, (g) calcium and/or lime compounds and (h) phosphate, and/or silicon oxide $20 / 80 - 80/20$ are still more preferably suitable. the compounding ratio of these (e), (f), (g), and (h) -- the weight ratio of solid content -- $(e)/(f) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. (e) -- $/(g)+(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. (f) -- $/(g)+(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- (g) -- $/(h) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable.

[0123] Here, the effectiveness by (e)/(f) and (e)/(g)+ (h) and (f)/(g)+ (h) compounding less than $1/99$ and then different self-repair effectiveness by exceeding $99/1$, respectively is not fully acquired. Moreover, if (g)/(h) has few calcium elution volumes, and cannot form only the protective film which blocks a corrosion origin less than by $1/99$ but $99/1$ is exceeded on the other hand Since silicon oxide required for making phosphoric-acid ion and calcium required starting the calcium and complexation reaction the calcium of the amount beyond the need not only being eluted, but adsorb for formation of a protective film is not fully supplied, sufficient self-repair effectiveness is not acquired.

[0124] (e) molybdate of the above (7), (f) triazoles, thiols, In one or more sorts of organic compounds chosen from thiadiazole, thiazoles, and thiurams, and the rust-proofing addition component which blended (i) calcium ion-exchange silica $20 / 80 - 80/20$ are still more preferably suitable. the compounding ratio of these (e), (f), and (i) -- the weight ratio of solid content -- $(e)/(f) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. (e) -- $/(i) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- (f) -- $/(i) = 1 / 99 - 99/1$ -- desirable -- $10 / 90 - 90/10$ -- $20 / 80 - 80/20$ are still more preferably suitable. Here, the effectiveness by (e)/(f) and (e)/(i) and (f)/(i) compounding less than $1/99$ and then different self-repair effectiveness by exceeding $99/1$, respectively is not fully acquired.

[0125] Loadings (the above-mentioned component (a) either of - (f)) of the above-mentioned rust-proofing addition component (Y) in the inside of an organic resin coat Or the loadings of the sum total of the self-repair nature manifestation matter which carried out compound addition of other components to the above (e) and/or (f) As opposed to the (Resultant X) (resultant with active hydrogen content compound (B) with which coat formation organic resin (A), part, or all compounds consist of hydrazine derivative (C) which has active hydrogen) 100 weight section (solid content) which is a resin constituent for coat formation The 1 - 100 weight section (solid content), desirable -- 5 - 80 weight section (solid content) -- it considers as 10 - 50 weight section (solid content) still more preferably. The corrosion-resistant improvement effectiveness has the small loadings of a rust-proofing addition component (Y) in under 1 weight section. On the other hand, if loadings exceed the 100 weight sections, since corrosion resistance will fall, it is not desirable.

[0126] Into an organic coat, it adds to the above-mentioned rust-proofing addition component. Moreover, as a corrosion inhibitor other oxide particles (for example, an aluminum oxide and a zirconium dioxide --) Molybdophosphate, such as titanium oxide, cerium oxide, and antimony oxide A (molybdophosphoric acid aluminum etc. and organic phosphorus) acid and its salt [for example,] for example, phytic acid, a phytic acid salt, phosphonic acid, and phosphonate -- And these metal salts, an alkali-metal salt, an alkaline earth metal salt, etc. can add one sort, such as organic inhibitor (for example, a hydrazine derivative, thiol compounds, dithiocarbamate, etc.), or two sorts or more.

[0127] Into an organic coat, further, if needed, solid lubricant (Z) can be blended in order to raise the workability of a coat. As solid lubricant (Z) applicable to this invention, the following is mentioned and these one sort or two sorts or more can be used, for example. .

(1) The Pori polyvinyl fluoride, the (2) fluoro-resin particle; for example, poly fluoro ethylene resin, (Pori polytetrafluoroethylene resin etc.), such as polyolefine wax and paraffin wax; for example, polyethylene wax, synthetic paraffin, native paraffin, micro wax, and a chlorinated hydrocarbon, polyvinylidene fluoride resin [0128], etc. moreover -- in addition, a fatty-acid amide system compound (for example, octadecanamide --) A palmitic-acid amide, methylenebisstearamide, ethylene-bis-stearamide, Oleic amide, an ESHIRU acid amide, an alkylene screw fatty-acid amide, etc., metal soap (for example, calcium stearate and lead stearate --) One sort, such as metallic sulfide (for example, molybdenum disulfide, tungsten disulfide, etc.), graphite, and graphites fluoride, such as lauric-acid calcium and palmitic-acid calcium, boron nitride, a polyalkylene glycol, and an alkali-metal sulfate, or two sorts or more may be used.

[0129] Also in the above solid lubricant, polyethylene wax and a fluoro-resin particle (even inside Pori polytetrafluoroethylene resin particle) are suitable especially. as polyethylene wax -- auction dust by Hoechst A.G. for example 9615A and auction dust 3715 and auction dust 3620 and auction dust 3910 and Mitsuhiro -- Formation -- Sun Wacks of make 131-P and Sun Wacks CHEMIPEARL made from 161-P and Mitsui Petrochemistry W-100 and CHEMIPEARL W-200, CHEMIPEARL W-500, and CHEMIPEARL W-800 and CHEMIPEARL W-950 etc. can be used.

[0130] Moreover, as a fluoro-resin particle, a tetrafluoroethylene particle is the most desirable, for example, it is RUBURON by Daikin Industries, LTD. L-2, RUBURON L-5, Mitsui and 1200 by E. I. du Pont de Nemours & Co., Fluon dispersion by Asahi-ICI Fluoropolymers Co., Ltd. AD1, Fluon dispersion AD2, Fluon L141J, Fluon L150J, Fluon L155J etc. are suitable. [MP1100 and MP1200] Moreover, the lubrication effectiveness which was excellent with especially concomitant use of a polyolefine wax and a tetrafluoroethylene particle is expectable in these.

[0131] the (Resultant X) (resultant with active hydrogen content compound (B) with which coat formation organic resin (A), part, or all compounds consist of hydrazine derivative (C) which has active hydrogen) 100 weight section (solid content) whose loadings of the solid lubricant (Z) in the inside of an organic coat are a resin constituent for coat formation -- receiving -- 1 - 80 weight section (solid content) -- it considers as 3 - 40 weight section (solid content) preferably. The lubrication effectiveness is deficient in the loadings of solid lubricant (Z) in under 1 weight section, and since paintwork will fall on the other hand if loadings exceed 80 weight sections, it is not desirable.

[0132] The organic coat which the organic covering steel plate of this invention has uses as a principal component a resultant (X) and a (resin constituent) with the active hydrogen content compound (B) with which coat formation organic resin (A), a part, or all compounds usually consist of a hydrazine derivative (C) which has active hydrogen. (a) calcium ion-exchange silica and phosphate which are the self-repair nature manifestation matter at this, (b) calcium ion-exchange silica, phosphate and silicon oxide, the (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiadiazole, and thiazoles one or more sorts of organic compounds chosen from thiurams, and **, although the rust-proofing addition component (Y) which carried out compound addition of other components is blended with inner either or the above (e), and/or (f) and solid lubricant (Z), a curing agent, etc. are added if needed further -- the need -- responding -- as an additive -- an organic color pigment (for example, a condensed multi-ring system organic pigment --) coloring colors (for example, organic solvent fusibility azo dye --), such as a phthalocyanine system organic pigment Inorganic pigments, such as a water-soluble azo metal color (for example, titanium oxide etc.), chelating agents (for example, thiol etc.) and a conductive pigment (for example, zinc --) Metal powder, such as aluminum and nickel, Lynn-ized iron, antimony dope mold tin oxide, etc. can add one sort, such as coupling agents (for example, a silane coupling agent, a titanium coupling agent, etc.) and a melamine cyanuric acid addition product, or two sorts or more.

[0133] Moreover, the coating constituent containing the above-mentioned principal component and an addition component for coat formation usually contains a solvent (an organic solvent and/or water), and a neutralizer etc. is added further if needed. If it can dissolve or distribute and the resultant (X) of the above-mentioned coat formation organic resin (A) and an active hydrogen content compound (B) can be adjusted as a coating constituent as the above-mentioned organic solvent, there is no special constraint,

for example, the various organic solvents illustrated previously can be used. The above-mentioned neutralizer is blended if needed, in order to neutralize and aqueous-ize coat formation organic resin (A), and when coat formation organic resin (A) is cationic resin, acids, such as an acetic acid, a lactic acid, and formic acid, can be used for it as a neutralizer.

[0134] An organic coat which was described above is formed in the upper part of the above-mentioned multiple oxide coat. The desiccation thickness of an organic coat sets preferably 0.3-3-micrometer 0.1-5 micrometers to 0.5-2 micrometers still more preferably. The thickness of an organic coat has the insufficient corrosion resistance of less than 0.1 micrometers, and on the other hand, if thickness exceeds 5 micrometers, conductivity and workability will fall. Moreover, it is appropriate to make coating weight of an organic coat into two or more 0.15 g/m and less than two 0.5 g/m preferably two or more 0.1 g/m and less than two 0.5 g/m to obtain advanced conductivity and spot welding nature with corrosion resistance. The coating weight of an organic coat has the insufficient corrosion resistance of less than two 0.1 g/m, and, on the other hand, the very advanced conductivity and spot welding nature which coating weight considers as a request in two or more 0.5 g/m are not obtained.

[0135] the multiple oxide coat (a component (alpha), the component (beta) in the amount of P2O5 conversions, and Mg --) with which are satisfied of this invention conditions which become a galvanized steel sheet from the constituent for the 1st layer coats of No.1 of Table 2 and 3 on a front face Sum total coating weight of the component (gamma) in the amount of metal conversions of Mn and aluminum : 359 mg/m² is formed. About the organic covering steel plate in which the organic coat which consists of a constituent for coats which carried out 15 weight sections combination of the rust-proofing addition component of No.15 of Table 5 to the solid content 100 weight section of the resin constituent for the 2nd layer coats of No.1 of Table 4 (base resin: thermosetting epoxy resin) was formed in the upper part The result of having investigated the relation of the coating weight of an organic coat and conductivity same with drawing 2 for the result of having investigated the relation between the coating weight of an organic coat and spot welding nature for the result of having investigated the relation between the coating weight of an organic coat and corrosion resistance, as well as drawing 1 is shown in drawing 3 , respectively. In addition, corrosion resistance performed the compound corrosion test (CCT) which evaluated white-rust-proof in [the example 1], and evaluated it by the same valuation basis as [an example 1] based on the rate of white rust generating area after 20 cycles. Moreover, the trial same about spot welding nature and conductivity as [an example 2] was performed, and the same valuation basis estimated.

[0136] According to drawing 1 , corrosion resistance to the extent that the coating weight of an organic coat increases improves, and by making coating weight into two or more 0.15 g/m preferably two or more 0.1 g/m shows that good corrosion resistance is acquired. On the other hand, if the coating weight of an organic coat becomes two or more 0.5 g/m according to drawing 2 , spot welding nature (spot continuation RBI nature) will fall rapidly, and conductivity is also known by getting worse rapidly when the coating weight of an organic coat becomes two or more 0.5 g/m according to drawing 3 . In order to obtain the outstanding corrosion resistance, especially advanced conductivity, and spot welding nature from the above reason, it is appropriate to make coating weight of an organic coat into two or more 0.15 g/m and less than two 0.5 g/m preferably two or more 0.1 g/m and less than two 0.5 g/m.

[0137] Next, the manufacture approach of the organic covering steel plate of this invention is explained. After the organic covering steel plate of this invention processes the front face of a zinc system plating steel plate or an aluminum system plating steel plate with the processing liquid containing the constituent of the multiple oxide coat mentioned above (processing liquid is applied), Carry out stoving and a resultant (X) with the active hydrogen content compound (B) with which the coat formation organic resin (A) mentioned above, a part, or all compounds consist of a hydrazine derivative (C) which has active hydrogen subsequently to the upper layer is included (it considers as a principal component preferably). To this, (a) calcium ion-exchange silica and phosphate, (b) calcium ion-exchange silica, Phosphate and silicon oxide, the (c) lime compound, and silicon oxide, (d) A lime compound, phosphate and silicon oxide, (e) molybdate, (f) Triazoles, thiols, thiadiazole, and thiazoles one or more sorts of organic compounds chosen from thiurams, and ** -- inner either Or it is manufactured by applying and

carrying out stoving of the coating constituent with which the rust-proofing addition component (Y) which carried out compound addition of other components was added by the above (e) and/or (f), and solid lubricant (Z) etc. was added further if needed. In addition, in order that the front face of a plating steel plate may carry out alkaline-degreasing processing if needed and may raise adhesion and corrosion resistance further before it applies the above-mentioned processing liquid, it can pretreat surface control processing etc.

[0138] In order to process the front face of a zinc system plating steel plate or an aluminum system plating steel plate with processing liquid and to form a multiple oxide coat (**) -- an oxide particle and (**) -- a phosphoric acid and/or a phosphoric-acid compound, and Mg (Ha) -- The metal ion of the either Mn or the aluminum, the water-soluble ion containing at least one sort in said metal, One or more sorts chosen from the groups which consist of a compound containing at least one sort in said metal, and a conjugated compound containing at least one sort in said metal, It contains, and processes with the processing liquid (water solution) which added each addition component (an organic resinous principle, an iron-group metal ion, a corrosion inhibitor, other additives) further mentioned above if needed, and an appropriate thing [carrying out afterbaking desiccation] is desirable.

[0139] here -- as the above-mentioned processing liquid -- the mol concentration of said addition component (**), the sum total mol concentration of 2OP5 conversion of said addition component (**), and the sum total mol concentration of the amount conversion of metals of said metal of said addition component (Ha) -- mole-ratio (**) -- $/(Ha) = 0.1-20$ and the processing liquid adjusted so that $0.1-10$, and a mole ratio $(Ha) / (b) = 0.1-1.5$ might be satisfied preferably are used. said mole-ratio (**) -- if $/(Ha)$ is not fully obtained less than by 0.1 but the addition effectiveness of an oxide particle exceeds 20 on the other hand, an oxide particle will check the eburnation of a coat. Moreover, effectiveness is not fully acquired for the above-mentioned mole ratio $(Ha)/(b)$ by addition of metal components, such as Mg, less than by 0.1 , but on the other hand, if 1.5 is exceeded, processing liquid ammonia quality will fall.

[0140] As an oxide particle which is addition component (**), silicon oxide (SiO_2 particle) is the most desirable. This silicon oxide can use a commercial silica sol, water-dispersion silicic-acid oligomer, etc. in processing liquid that what is necessary is just a stable water-dispersion silica particle. However, as for fluorides, such as a hexafluorosilicic acid, corrosive is strong, and since the effect on the body is also large, it is desirable [fluorides] not to use it from viewpoints, such as effect on work environment. the addition (in the case of silicon oxide, it is an addition as SiO_2 amount) of the oxide particle in the inside of processing liquid -- $0.001-3.0\text{mol/L}$ -- it is preferably appropriate $0.05-1.0\text{mol/L}$, and to be referred to as $0.1-0.5\text{mol/L}$ still more preferably. Under 0.001 mols / L are not enough as the effectiveness according [the addition of an oxide particle] to addition, and there is an inclination for corrosion resistance to be inferior. On the other hand, if an addition exceeds 3.0 mols / L , the water resisting property of a coat will worsen, and there is an inclination for corrosion resistance to also deteriorate as a result.

[0141] As the phosphoric acid which is addition component (b), and/or a phosphoric-acid compound Polyphosphoric acid, such as orthophosphoric acid, a pyrophosphoric acid, and the Tripoli phosphoric acid, metaphosphoric acids, and these mineral salt For example, (the first aluminium phosphate etc. and phosphorous acid), phosphite, The anion produced when compounds of phosphoric-acid content, such as hypophosphorous acid and hypophosphite, dissolve in a water solution, Or the gestalt which exists as complex ion with a metal cation, the gestalt which exists as a free acid, The amount of the phosphoric-acid component in this invention specifies the sum total of all these [which exist in processing liquid] gestalten as 2OP5 conversion including all, such as a gestalt which exists in the state of moisture powder as mineral salt.

[0142] the addition of the phosphoric acid in the inside of processing liquid, and/or a phosphoric-acid compound -- 2OP5 conversion -- $0.001-6.0\text{mol/L}$ -- it is preferably appropriate $0.02-1.0\text{mol/L}$, and to be referred to as $0.1-0.8\text{mol/L}$ still more preferably. Under 0.001 mols / L are not enough as the effectiveness according [the addition of a phosphoric acid and/or a phosphoric-acid compound] to addition, and there is an inclination for corrosion resistance to be inferior. if an addition, on the other hand, exceeds 6.0 mols / L -- superfluous phosphoric-acid ion -- a humid environment -- setting -- a

plating coat -- reacting -- corrosive environment -- the corrosion of a plating base -- promoting -- discoloration and silverfish -- it becomes the factor of the ** rust generating. Moreover, since the corrosion resistance outstanding multiple oxide can be obtained as addition component (b), it is also effective to use an ammonium phosphate salt. As an ammonium phosphate salt, it is desirable to use one sort, such as monobasic ammonium phosphate and dibasic calcium phosphate, or two sorts or more.

[0143] Although a compound and a conjugated compound are sufficient as an existence-in processing liquid of addition component (Ha) gestalt, in order to acquire the especially excellent corrosion resistance, especially the gestalt of the water-soluble ion with which the metal ion of Mg, Mn, and aluminum or the metal of Mg, Mn, and aluminum is contained is desirable. In addition, in order to supply the ion of an addition component (Ha) as a metal salt, anions, such as a chlorine ion, nitrate ion, sulfate ion, acetic-acid ion, and boric-acid ion, may be added in processing liquid. The amount of the component of Mg, Mn, and aluminum in this invention specifies the sum total of all these [which exist in processing liquid] gestalten as amount conversion of metals. It is appropriate for the addition of the above-mentioned addition component (Ha) in the inside of processing liquid 0.001-3.0mol/L, and to be preferably referred to as 0.01-0.5mol/L in the sum total of the amount conversion of metals. The effectiveness according [the addition of these sum totals] to addition is not fully acquired, but on the other hand, if an addition exceeds 3.0 mols / L, these components will come to check the network of a coat conversely, and a precise coat will become impossible in less than 0.001 mols easily. Moreover, a metal component becomes easy to be eluted from a coat, and the defect of an appearance discoloring depending on an environment is produced.

[0144] In processing liquid, as addition component (d), further The metal ion of the nickel, Fe, or the Co (es), By being able to carry out optimum dose addition of the one or more sorts chosen from the groups which consist of water-soluble ion containing at least one sort in said metal, and adding such an iron-group metal The black discoloration phenomenon resulting from the corrosion of the plating outermost layer under a humid environment produced when not adding an iron-group metal is avoidable. Moreover, the effectiveness of nickel is high also especially in these iron-group metals, and the effectiveness excellent also in the minute amount is accepted. However, since superfluous addition of iron-group metals, such as nickel and Co, leads to corrosion-resistant degradation, addition of optimum dose is required for it.

[0145] As an addition of the above-mentioned addition component (**), it is the amount conversion of metals and it is desirable 1 / to make 10000-1 mol into 1 / the range of 10000 - 1/100 mol desirably to one mol (Ha) of addition components in the amount conversion of metals. If less than 1/10000 mol is not enough as the effectiveness according [the addition of addition component (**)] to addition and an addition exceeds one mol on the other hand to one mol (Ha) of addition components, corrosion resistance will deteriorate as mentioned above. Into processing liquid, optimum dose addition of the addition component to the inside of the coat described previously may be carried out besides the above-mentioned addition component (b) - (d). It is appropriate 0.5-5, and to set pH of processing liquid (water solution) to 2-4 preferably. Since the reactivity of processing liquid becomes [processing liquid] high too much by less than 0.5 pH, a detailed defective part is formed in a coat, and corrosion resistance falls. On the other hand, if processing liquid exceeds pH5, the reactivity of processing liquid will become low, it becomes inadequate joining [of the interface of a plating coat and a multiple oxide coat] together, and there is an inclination for corrosion resistance to fall also in this case.

[0146] As an approach of coating a plating steel plate front face with processing liquid, any of a spreading method, an immersion method, and a spray method are sufficient, and which spreading means, such as roll coaters (3 roll methods, 2 roll methods, etc.), a squeeze coating machine, and a die coating machine, may be used by the spreading method. Moreover, it is also possible to perform adjustment of coverage, equalization of an appearance, and equalization of thickness by the air knife method or the roll extracting method after the spreading processing by a squeeze coating machine etc., immersion processing, and spray processing. Although there is no constraint special to the temperature of processing liquid, about ordinary temperature -60 degree C is suitable. Below in ordinary temperature, since the facility for cooling etc. is needed, it is uneconomical, and on the other hand, since moisture

will become easy to evaporate if it exceeds 60 degrees C, management of processing liquid becomes difficult.

[0147] After coating processing liquid as mentioned above, stoving is usually performed, without rinsing, but the processing liquid used by this invention may rinse after processing in order to form a poorly soluble salt by the reaction with a substrate plating steel plate. The approach of carrying out stoving of the coated processing liquid is arbitrary, for example, can use the means of a dryer, an air-heating furnace, a high-frequency-induction-heating furnace, an infrared furnace, etc. As for this stoving processing, it is desirable to perform desirably 80-200-degrees C 50-300 degrees C in 80-160 degrees C still more desirably by attainment board temperature. At less than 50 degrees C, moisture remains so much into a coat and stoving temperature becomes inadequate [corrosion resistance]. On the other hand, if stoving temperature exceeds 300 degrees C, it is not only noneconomic, but it will become easy to produce a defect in a coat, and corrosion resistance will fall.

[0148] After forming a multiple oxide coat in the front face of a zinc system plating steel plate or an aluminum system plating steel plate as mentioned above, the coating constituent for organic coat formation is applied to the upper layer. As an approach of applying a coating constituent, the approach of arbitration, such as the applying method, dip coating, and a spray method, is employable. As an applying method, which approaches, such as roll coaters (3 roll methods, 2 roll methods, etc.), a squeeze coating machine, and a die coating machine, may be used. Moreover, it is also possible to perform adjustment of coverage, equalization of an appearance, and equalization of thickness by the air knife method or the roll extracting method after the spreading processing by a squeeze coating machine etc., immersion processing, or spray processing.

[0149] Although stoving is performed after spreading of a coating constituent, without usually rinsing, a rinsing process may be carried out after spreading of a coating constituent. A dryer, an air-heating furnace, a high-frequency-induction-heating furnace, an infrared furnace, etc. can be used for stoving processing. As for heat-treatment, it is desirable to perform 50-350 degrees C in 80 degrees C - 250 degrees C preferably by attainment board temperature. At less than 50 degrees C, the moisture in a coat remains so much and whenever [stoving temperature] becomes inadequate [corrosion resistance]. Moreover, when whenever [stoving temperature] exceeds 350 degrees C, there is a possibility it is not only noneconomic, but that a defect may arise in a coat and corrosion resistance may fall.

[0150] This invention contains the steel plate which has a coat which was described above on both sides or one side. Therefore, as a gestalt of this invention steel plate, there is the following, for example.

(1) one side: -- a plating coat-multiple oxide coat-organic coat and an one side:plating coat (2) one side:plating coat-multiple oxide coat-organic coat -- one side: -- plating coat-well-known double-sided [phosphate processing coat etc.] (3): -- plating coat-multiple oxide coat-organic coat (4) one side: -- a plating coat-multiple oxide coat-organic coat -- one side: -- plating coat-multiple oxide coat (5) one side: -- a plating coat-multiple oxide coat-organic coat and an one side:plating coat-organic coat [0151]

[Example] The processing liquid for the 1st layer coat formation (coat constituent) shown in [example 1] Table 2 and 3 was adjusted. Moreover, it is the following, and the resin constituent for the 2nd layer coat formation (resultant) was made and compounded.

Taught the [synthetic example 1] EP828 (oil-ized shell epoxy company make, weight per epoxy equivalent 187) 1870 section, the bisphenol A 912 section, the tetraethylammonium star's picture 2 section, and the methyl-isobutyl-ketone 300 section to the 4 opening flask, and carried out the temperature up to 140 degrees C, it was made to react for 4 hours, and weight per epoxy equivalent 1391 and the epoxy resin of 90% of solid content were obtained. while cooling at 100 degrees C, and cooling 3 and 5-dimethylpyrazol (molecular weight 96) after making the 96 sections and dibutyl amine (molecular weight 129) react for 6 hours until the 129 sections, in addition an epoxy group disappear after adding the ethylene-glycol-monobutyl-ether 1500 section to this thing -- the methyl-isobutyl-ketone 205 section -- in addition, the pyrazole modified epoxy resin of 60% of solid content was obtained. Let this be a resin constituent (1). the hydrazine derivative (C) with which this resin constituent (1) has coat formation organic resin (A) and active hydrogen -- 50-mol% -- it is a resultant with the included active hydrogen content compound.

[0152] The [synthetic example 2] EP1007 (oil-ized shell epoxy company make, weight per epoxy equivalent 2000) 4000 section and the ethylene-glycol-monobutyl-ether 2239 section were taught to the 4 opening flask, the temperature up was carried out to 120 degrees C, and the epoxy resin was dissolved completely in 1 hour. This thing was cooled at 100 degrees C, the methyl-isobutyl-ketone 540 section was added cooling it, after making 3-amino-1,2,4-triazole (molecular weight 84) react for 6 hours until the 168 sections, in addition an epoxy group disappeared, and the triazole conversion epoxy resin of 60% of solid content was obtained. Let this be a resin constituent (2). the hydrazine derivative (C) with which this resin constituent (2) has coat formation organic resin (A) and active hydrogen -- 100-mol% -- it is a resultant with the included active hydrogen content compound.

[0153] The [synthetic example 3] isophorone diisocyanate (isocyanate equivalent 111) 222 section and the methyl-isobutyl-ketone 34 section were taught to the 4 opening flask, it kept at 30-40 degrees C, the methylethyl ketoxime (molecular weight 87) 87 section was kept at 40 degrees C after dropping over 3 hours for 2 hours, and the isocyanate equivalent 309 and the regional block isocyanate of 90% of solid content were obtained.

[0154] Subsequently, taught the EP828 (oil-ized shell epoxy company make, weight per epoxy equivalent 187) 1496 section, the bisphenol A 684 section, the tetraethylammonium star's picture 1 section, and the methyl-isobutyl-ketone 241 section to the 4 opening flask, and carried out the temperature up to 140 degrees C, it was made to react for 4 hours, and weight per epoxy equivalent 1090 and the epoxy resin of 90% of solid content were obtained. After adding the methyl-isobutyl-ketone 1000 section to this thing, it cools at 100 degrees C, and it is 3-mercapto. - After making 1, 2, and 4-triazole (molecular weight 101) react for 6 hours until the 202 sections, in addition an epoxy group disappeared, the regional block isocyanate of the 90% of the above-mentioned solid content was made to react at 100 degree C of 230 ***** for 3 hours, and it checked that the isocyanate radical had disappeared. Furthermore, the ethylene-glycol-monobutyl-ether 461 section was added, and the triazole conversion epoxy resin of 60% of solid content was obtained. Let this be a resin constituent (3). the hydrazine derivative (C) with which this resin constituent (3) has coat formation organic resin (A) and active hydrogen -- 100-mol% -- it is a resultant with the included active hydrogen content compound.

[0155] Taught the [synthetic example 4] EP828 (oil-ized shell epoxy company make, weight per epoxy equivalent 187) 1870 section, the bisphenol A 912 section, the tetraethylammonium star's picture 2 section, and the methyl-isobutyl-ketone 300 section to the 4 opening flask, and carried out the temperature up to 140 degrees C, it was made to react for 4 hours, and weight per epoxy equivalent 1391 and the epoxy resin of 90% of solid content were obtained. After adding the ethylene-glycol-monobutyl-ether 1500 section to this thing, it cooled at 100 degrees C, and the methyl-isobutyl-ketone 225 section was added cooling it, after making dibutyl amine (molecular weight 129) react for 6 hours until the 258 sections, in addition an epoxy group disappeared, and the epoxy amine addition product of 60% of solid content was obtained. Let this be a resin constituent (4). This resin constituent (4) is a resultant of coat formation organic resin (A) and the active hydrogen content compound which does not contain the hydrazine derivative (C) which has active hydrogen.

[0156] the above -- the curing agent was blended with resin constituent (1) - (4) compounded by making it like, and the resin constituent (coating constituent) shown in Table 4 was created. The solid lubricant shown in the rust-proofing addition component (self-repair nature manifestation matter) shown in Table 5 (Table 5-1 and 5-2) and Table 6 was suitably blended with these coatings constituent, need time amount distribution was carried out using the disperser for coatings (Sand grinder), and it considered as the desired coating constituent.

[0157] In order to obtain household electric appliances, building materials, and the organic covering steel plate for autoparts, board thickness:0.8mm, The plating steel plate shown in Table 1 which performed various zinc system plating or aluminum system plating to Surface roughness Ra:1.0micrometer cold rolled sheet steel is used as a processing negative. After alkaline-degreasing-processing and rinsing drying the front face of this plating steel plate, stoving of the processing liquid (coat constituent) shown in Table 2 and 3 was applied and carried out by the roll coater, and the 1st layer coat was made to form. The solid content (heating residue) or the spreading conditions of processing

liquid (rolling force of a roll, rotational speed, etc.) adjusted the thickness of this 1st layer coat. Subsequently, applied the coating constituent shown in Table 4 by the roll coater, it carried out stoving, the 2nd layer coat was made to form, and the organic covering steel plate of the example of this invention and the example of a comparison was manufactured. The solid content (heating residue) or the spreading conditions of a coating constituent (rolling force of a roll, rotational speed, etc.) adjusted the thickness of the 2nd layer coat.

[0158] About the obtained organic covering steel plate, the quality engine performance (a coat appearance, white-rust-proof, the white-rust-proof after alkaline degreasing, coating adhesion, workability) was evaluated. The result is shown in Table 7 - 39 with the coat configuration of the 1st layer coat and the 2nd layer coat etc. Evaluation of the quality engine performance of an organic covering steel plate was performed by [as being the following].

[0159] (1) The homogeneity (existence of nonuniformity) of a coat appearance was evaluated by viewing about coat appearance each sample. The valuation basis is as follows.

O : the appearance in which the appearance x:nonuniformity in which nonuniformity completely twists and uniform appearance **:nonuniformity is conspicuous a little is conspicuous [0160] (2) The compound corrosion test (CCT) shown below about white-rust-proof each sample was performed, and the rate of white rust generating area after a predetermined cycle estimated.

[The contents of 1 cycle of a compound corrosion test (CCT)]

3wt% salt spray test (30 degree-C;0.5 hour)

** humidity cabinet test (30 degrees C, 95%RH; 1.5 hours)

** hot-air-drying trial (50 degrees C, 20%RH; 2.0 hours)

** hot-air-drying trial (30 degrees C, 20%RH; 2.0 hours)

The valuation basis is as follows.

O O[:-white-rust-generating-less]+: Less than [5% of rates of white rust generating area] O : 5% or more of rates of white-rust generating area, 10% or more of rates of less than 10%O:-white-rust area, less-than [25%] ** : 25% or more of rates of white rust generating area, less than [50%] x : 50% or more of rates of white rust generating area [0161] (3) After performing alkaline degreasing by alkali treatment liquid CLN-364S (60 degrees C, spray 2 minutes) by Nihon Parkerizing Co., Ltd., the above-mentioned compound corrosion test (CCT) was performed, and the rate of white rust area after a predetermined cycle estimated white-rust-proof each sample after alkaline degreasing. The valuation basis is as follows.

O O[:-white-rust-generating-less]+: Less than [5% of rates of white rust generating area] O : 5% or more of rates of white-rust generating area, 10% or more of rates of less than 10%O:-white-rust generating area, less-than [25%] ** : 25% or more of rates of white rust generating area, less than [50%] x : 50% or more of rates of white rust generating area [0162] (4) After painting the baking paint (30 micrometers of thickness) of a melamine system, it was immersed into priming for 2 hours, the cut of the squares (it is the squares of 10x10 at intervals of 1mm) was put in immediately, attachment and exfoliation by adhesive tape were performed, and the stripped plane moment of a paint film estimated coating adhesion each sample. The valuation basis is as follows.

O 5% or more of less than 5% [of :-exfoliation-less O:stripped plane moments] **:stripped plane moments, less than [20%] x : 20% or more of stripped plane moments [0163] (5) Deep-drawing shaping (non-oiling conditions) was performed by diameter phiof workability blank120mm, and diameter phiof dice50mm, and shaping height until a crack arises estimated. The valuation basis is as follows.

O :diaphragm omission O:height [shaping / of 30mm or more] **:shaping height of 20mm or more, less than [30mm] x : shaping height of less than 20mm [0164]

[Table 1]

表 1

No.	種 類	付着量 (g/m ²)
1	電気亜鉛めっき鋼板	20
2	熔融亜鉛めっき鋼板	60
3	合金化熔融亜鉛めっき鋼板 (Fe:10wt %)	60
4	熔融 Zn-Al 合金めっき鋼板 (Al:55wt %)	90
5	熔融 Zn-5wt % Al-0.5wt % Mg 合金めっき鋼板	90
6	熔融アルミニウムめっき鋼板 (Al-6wt % Si 合金めっき)	60

[0165]

[Table 2]

表 2

[第一層皮膜用組成物]

No.	酸化物微粒子 (イ)		Mg, Mn, Al (ハ)		リン酸・リン酸化合物 (ロ)		有機樹脂	
	種 類	濃 度 (M/L)	種 類	濃 度 (M/L) *1	種 類	濃 度 (M/L) *2	種 類	濃 度 (g/l)
1	コロイダルシリカ	0.3	Mn	0.10	オルトリン酸	0.20	—	—
2	コロイダルシリカ	0.04	Mn	0.10	オルトリン酸	0.20	—	—
3	コロイダルシリカ	0.3	Mn	0.10	オルトリン酸	0.50	—	—
4	コロイダルシリカ	0.33	Mn	0.11	オルトリン酸	0.10	—	—
5	コロイダルシリカ	1.8	Mn	0.10	オルトリン酸	0.20	—	—
6	コロイダルシリカ	0.3	Mn	0.10	オルトリン酸	0.20	アクリルースチレン系水分散性樹脂	180
7	コロイダルシリカ	0.3	Al	0.10	オルトリン酸	0.20	—	—
8	コロイダルシリカ	0.04	Al	0.10	オルトリン酸	0.20	—	—
9	コロイダルシリカ	0.3	Al	0.10	オルトリン酸	0.50	—	—
10	コロイダルシリカ	0.3	Al	0.10	オルトリン酸	0.20	—	—
11	コロイダルシリカ	0.33	Al	0.11	オルトリン酸	0.10	—	—
12	アルミナゾル	0.3	Al	0.10	オルトリン酸	0.20	—	—
13	コロイダルシリカ	0.3	Mg	0.10	オルトリン酸	0.20	—	—
14	—	—	Mn	0.10	オルトリン酸	0.20	—	—
15	—	—	Al	0.10	オルトリン酸	0.20	—	—
16	—	—	Mg	0.10	オルトリン酸	0.20	—	—
17	コロイダルシリカ	0.3	—	—	オルトリン酸	0.20	—	—
18	コロイダルシリカ	0.3	Mn	0.10	—	—	—	—
19	コロイダルシリカ	0.3	Al	0.10	—	—	—	—
20	コロイダルシリカ	0.3	Mg	0.10	—	—	—	—
21	リチウムシリケート	1.0	—	—	—	—	—	—

*1 Mg, Mn, Al の金属量換算の合計モル濃度

*2 P₂O₅換算の合計モル濃度

[0166]

[Table 3]

表 3

No.	モル比 (イ)/(ハ)	モル比 (ハ)/(ロ)	本発明条件の適否 * 3
1	3.0	0.5	○
2	0.4	0.5	○
3	3.0	0.2	○
4	3.0	1.1	○
5	18.0	0.5	○
6	3.0	0.5	○
7	3.0	0.5	○
8	0.4	0.5	○
9	3.0	0.2	○
10	3.0	1.1	○
11	18.0	0.5	○
12	3.0	0.5	○
13	3.0	0.5	○
14	—	0.5	×
15	—	0.5	×
16	—	0.5	×
17	—	—	×
18	3.0	—	×
19	3.0	—	×
20	3.0	—	×
21	—	—	×

* 3 ○：本発明条件を満足する

×：本発明条件を満足しない

[0167]

[Table 4]

表 4

〔第二層皮膜用樹脂組成物〕

No.	基 体 樹 脂		硬 化 剤		触 媒	本発明条件 の適否
	種類 *1	配合量	種類 *2	配合量		
1	(1)	100 部	A	5 部	ジブチル錫ジラウレート (0.2 部)	満足する
2	(1)	100 部	B	25 部	ジブチル錫ジラウレート (1.0 部)	満足する
3	(1)	100 部	C	25 部	—	満足する
4	(2)	100 部	A	50 部	ジブチル錫ジラウレート (2.0 部)	満足する
5	(2)	100 部	B	50 部	ジブチル錫ジラウレート (3.0 部)	満足する
6	(2)	100 部	C	80 部	ジブチル錫ジラウレート (4.0 部)	満足する
7	(3)	100 部	A	25 部	ナフテン酸コバルト (1.0 部)	満足する
8	(3)	100 部	B	10 部	塩化第一錫 (1.0 部)	満足する
9	(3)	100 部	C	50 部	N-エチルモルホリン (1.0 部)	満足する
10	(1)	100 部	D	25 部	—	満足する
11	(3)	100 部	D	30 部	—	満足する
12	(4)	100 部	B	25 部	ジブチル錫ジラウレート (1.0 部)	満足しない
13	ヒドラジン誘導体水溶液 (3,5-ジメチルピラゾールの 5wt% 水溶液)					満足しない
14	エポキシアミン付加物とヒドラジン誘導体の混合物 (樹脂組成物 No. 12 に 3,5-ジメチルピラゾールを基体樹脂 100 重量部に対して 3 重量部添加し、 攪拌したもの)					満足しない

*1 明細書本文に記載の合成例 1～4 で合成された樹脂組成物 (1)～(4)

*2 A: IPDI の MEK オキシムブロック体: 武田薬品工業製 “タケネート B-870N”

B: イソシヌレートタイプ: Bayer 社製 “DESMODUR BL-3175”

C: HMDI の MEK オキシムブロック体: 旭化成工業製 “デュラネート MF-B80M”

D: イミノ基型メラミン樹脂: 三井サイテック製 “サイメル 325”

[0168]

[Table 5]

表 5-1

No.	防錆添加成分 (自己補修性発現物質)			配合比*1
	(a) Ca イオン交換シリカ + リン酸塩 (b) Ca イオン交換シリカ + リン酸塩 + 酸化ケイ素 (c) カルシウム化合物 + 酸化ケイ素 (d) カルシウム化合物 + リン酸塩 + 酸化ケイ素 (g), (h), (i) その他の成分	(e) モリブデン酸塩	(f) トリアゾール類, チオール類, チアジアゾール類, チアゾール類, チウラム類の中から選ばれる1種以上の有機化合物	(a) ~ (d), (g) ~ (i) : (e) : (f)
1	Ca イオン交換シリカ + リン酸 Zn (配合比 1 : 1 *1)	—	—	—
2	Ca イオン交換シリカ + リン酸 Zn + シリカ (配合比 1 : 1 : 1 *1)	—	—	—
3	酸化 Ca + シリカ + トリポリリン酸二水素 Al (配合比 1 : 1 : 1 *1)	—	—	—
4	酸化 Ca + シリカ	—	—	—
5	—	リン酸 Mo 酸 Al	—	—
6	—	リン酸 Mo 酸 CaZn	—	—
7	—	—	5-アミノ-3-メルカプト-1,2,4-トリ アゾール	—
8	—	—	1,3,5-トリアジン-2,4,6-トリチオ- ール	—
9	—	—	5-アミノ-2-メルカプト-1,3,4-チア ジアゾール	—
10	—	—	2-メルカプトベンゾチアゾール	—
11	—	—	テトラエチルチウラムジスルフィ ド	—

*1 重量比

表 5-2

No.	防錆添加成分 (自己補修性発現物質)			配合比*1
	(a) Caイオン交換シリカ+リン酸塩 (b) Caイオン交換シリカ+リン酸塩+酸化ケイ素 (c) カルシウム化合物+リン酸塩+酸化ケイ素 (d) カルシウム化合物+リン酸塩+酸化ケイ素 (e) その他の成分 (f) (g), (h), (i) の成分 (配合比 1 : 1 + 1)	(e) モリブデン酸塩	(f) トリアゾール類, チオール類, チアジアゾール類, チアゾール類, チウラム類の中から選ばれた 1 種以上の有機化合物	
12	リン酸 Ca + トリポリリン酸二水素 Al (配合比 1 : 1 + 1)	リン酸 Mo 酸 Al	—	10 : 10 : 0
13	Caイオン交換シリカ	—	テトラエチルチウラムジスルフィド	10 : 0 : 10
14	—	リン酸 Mo 酸 Al	テトラエチルチウラムジスルフィド	0 : 10 : 10
15	ケイ酸 Ca + トリポリリン酸二水素 Al (配合比 1 : 1 + 1)	リン酸 Mo 酸 Al	テトラエチルチウラムジスルフィド	10 : 10 : 10
16	酸化 Ca + シリカ (配合比 1 : 1 + 1)	リン酸 Mo 酸 Al	—	10 : 10 : 0
17	Caイオン交換シリカ	リン酸 Mo 酸 Al	—	10 : 10 : 0
18	酸化 Ca + リン酸 Zn (配合比 1 : 1 + 1)	—	テトラエチルチウラムジスルフィド	10 : 0 : 10
19	酸化 Ca + シリカ (配合比 1 : 1 + 1)	—	テトラエチルチウラムジスルフィド	10 : 0 : 10
20	酸化 Ca + シリカ (配合比 1 : 1 + 1)	リン酸 Mo 酸 Al	テトラエチルチウラムジスルフィド	10 : 10 : 10
21	Caイオン交換シリカ	リン酸 Mo 酸 Al	テトラエチルチウラムジスルフィド	10 : 10 : 10

*1 重量比

[0169]

[Table 6]

表 6

[固形潤滑剤]

No.	種 類	商 品 名
1	ポリエチレンワックス	日本精糖製 “LUVAX1151”
2	ポリエチレンワックス	セリダスト製 “3620”
3	ポリエチレンワックス	三井石油化学製 “ケミパール W-100”
4	テトラフルオロエチレン樹脂	三井・デュポン製 “MP1100”
5	テトラフルオロエチレン樹脂	ダイキン工業製 “L-2”
6	No. 1 と No. 4 の混合物 (混合比 = 1 : 1)	—

[0170] Following Table 7 - 39 is indicated to front Naka. *1-*7 The following contents are shown.

*1: The plating steel plate No given in Table 1

*2: The constituent No for the 1st layer coats given in Table 2 and 3

*3: A component (beta) is the coating weight of 2OP5 conversion, and a component (gamma) is the resin constituent No for the 2nd layer coats given in the coating weight *4:table 4 of the amount conversion of metals of Mg, Mn, and aluminum.

*5: The rust-proofing addition component No given in Table 5

*6: Solid lubricant No given in Table 6

*7: Loadings to the solid content 100 weight section of a resin constituent (weight section)

[0171]

[Table 7]

表 7

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜 組成物	乾燥 温度 (℃)	膜厚 (μ m)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
1	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
2	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
3	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
4	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
5	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
6	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
7	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
8	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
9	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
10	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
11	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
12	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
13	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
14	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例

[0172]

[Table 8]

表 8

No.	第二層皮膜							区 分
	樹脂組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥温度 (℃)	膜厚 (μm)	
		種類 *4	配合量 *5	種類 *6	配合量 *7			
1	1	15	15	—	—	140	1.0	本發明例
2	2	15	15	—	—	140	1.0	本發明例
3	3	15	15	—	—	140	1.0	本發明例
4	4	15	15	—	—	140	1.0	本發明例
5	5	15	15	—	—	140	1.0	本發明例
6	6	15	15	—	—	140	1.0	本發明例
7	7	15	15	—	—	140	1.0	本發明例
8	8	15	15	—	—	140	1.0	本發明例
9	9	15	15	—	—	140	1.0	本發明例
10	10	15	15	—	—	140	1.0	本發明例
11	11	15	15	—	—	140	1.0	本發明例
12	12	15	15	—	—	140	1.0	比較例
13	13	15	15	—	—	140	1.0	比較例
14	14	15	15	—	—	140	1.0	比較例

[0173]

[Table 9]

表 9

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加工 性	
1	○	◎	◎	◎	—	本発明例
2	○	◎	◎	◎	—	本発明例
3	○	◎	◎	◎	—	本発明例
4	○	◎	◎	◎	—	本発明例
5	○	◎	◎	◎	—	本発明例
6	○	◎	◎	◎	—	本発明例
7	○	◎	◎	◎	—	本発明例
8	○	◎	◎	◎	—	本発明例
9	○	◎	◎	◎	—	本発明例
10	○	◎	◎	◎	—	本発明例
11	○	◎	◎	◎	—	本発明例
12	○	△	×	◎	—	比較例
13	○	×	×	×	—	比較例
14	○	△	×	◎	—	比較例

[0174]

[Table 10]

表 10

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					含 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
15	1	2	140	0.3	344	30	245	69	0.4	0.5	本発明例
16	1	3	140	0.3	363	90	245	28	3.0	0.2	本発明例
17	1	4	140	0.3	360	200	99	61	3.0	1.1	本発明例
18	1	5	140	0.3	358	290	53	15	18.0	0.5	本発明例
19	1	6	140	0.3	600	150	163	46	3.0	0.5	本発明例
20	1	7	140	0.3	358	160	174	24	3.0	0.5	本発明例
21	1	8	140	0.3	360	35	286	39	0.4	0.5	本発明例
22	1	9	140	0.3	349	90	245	14	3.0	0.2	本発明例
23	1	10	140	0.3	362	220	109	33	3.0	1.1	本発明例
24	1	11	140	0.3	362	300	54	8	18.0	0.5	本発明例

[0175]

[Table 11]

表 11

No.	第二層皮膜							区 分
	樹 脂 組成物	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 温度	膜厚	
		種類 *4	配合量 *5	種類 *6	配合量 *7			
15	1	15	15	—	—	140	1.0	本発明例
16	1	15	15	—	—	140	1.0	本発明例
17	1	15	15	—	—	140	1.0	本発明例
18	1	15	15	—	—	140	1.0	本発明例
19	1	15	15	—	—	140	1.0	本発明例
20	1	15	15	—	—	140	1.0	本発明例
21	1	15	15	—	—	140	1.0	本発明例
22	1	15	15	—	—	140	1.0	本発明例
23	1	15	15	—	—	140	1.0	本発明例
24	1	15	15	—	—	140	1.0	本発明例

[0176]

[Table 12]

表 1 2

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加 工 性	
15	○	◎	◎	◎	—	本発明例
16	○	◎	◎	◎	—	本発明例
17	○	◎	◎	◎	—	本発明例
18	○	◎	◎	◎	—	本発明例
19	○	◎	◎	◎	—	本発明例
20	○	◎	◎	◎	—	本発明例
21	○	◎	◎	◎	—	本発明例
22	○	◎	◎	◎	—	本発明例
23	○	◎	◎	◎	—	本発明例
24	○	◎	◎	◎	—	本発明例

[0177]

[Table 13]

表 1 3

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
25	1	12	140	0.3	358	160	174	24	3.0	0.5	本発明例
26	1	13	140	0.3	355	160	174	21	3.0	0.5	本発明例
27	1	14	140	0.3	362	—	283	79	—	0.5	比較例
28	1	15	140	0.3	360	—	316	44	—	0.5	比較例
29	1	16	140	0.3	355	—	316	39	—	0.5	比較例
30	1	17	140	0.3	358	334	24	—	—	—	比較例
31	1	18	140	0.3	353	270	—	83	3.0	—	比較例
32	1	19	140	0.3	357	310	—	47	3.0	—	比較例
33	1	20	140	0.3	363	320	—	43	3.0	—	比較例
34	1	21	140	0.3	360	—	—	—	—	—	比較例

[0178]

[Table 14]

表 14

No.	第二層皮膜							区 分
	樹 脂 組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度	膜厚	
		種類 *4	配合量 *5	種類 *6	配合量 *7			
25	1	15	15	—	—	140	1.0	本発明例
26	1	15	15	—	—	140	1.0	本発明例
27	1	15	15	—	—	140	1.0	比較例
28	1	15	15	—	—	140	1.0	比較例
29	1	15	15	—	—	140	1.0	比較例
30	1	15	15	—	—	140	1.0	比較例
31	1	15	15	—	—	140	1.0	比較例
32	1	15	15	—	—	140	1.0	比較例
33	1	15	15	—	—	140	1.0	比較例
34	1	15	15	—	—	140	1.0	比較例

[0179]

[Table 15]

表 15

No.	性 能					区 分
	外観	耐白錆性 CCT	アルカリ脱脂 後の耐白錆性 CCT	塗 装 密着性	加工 性	
		50 サイクル後	50 サイクル後			
25	○	○+	○+	◎	—	本発明例
26	○	○	○	○	—	本発明例
27	○	△	△	△	—	比較例
28	○	△	△	△	—	比較例
29	○	△	△	△	—	比較例
30	○	△	△	○	—	比較例
31	○	△	×	○	—	比較例
32	○	△	×	○	—	比較例
33	○	△	×	○	—	比較例
34	○	△	×	△	—	比較例

[0180]

[Table 16]

表 16

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜 組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
35	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
36	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
37	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
38	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
39	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
40	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
41	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
42	2	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
43	3	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
44	4	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
45	5	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
46	6	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0181]

[Table 17]

表 17

No.	第二層皮膜							区 分
	樹 脂 組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度	膜厚	
		種類 *4	配合量 *5	種類 *6	配合量 *7			
35	1	—	—	—	—	140	1.0	比較例
36	1	15	1	—	—	140	1.0	本發明例
37	1	15	5	—	—	140	1.0	本發明例
38	1	15	25	—	—	140	1.0	本發明例
39	1	15	50	—	—	140	1.0	本發明例
40	1	15	100	—	—	140	1.0	本發明例
41	1	15	150	—	—	140	1.0	比較例
42	1	15	15	—	—	140	1.0	本發明例
43	1	15	15	—	—	140	1.0	本發明例
44	1	15	15	—	—	140	1.0	本發明例
45	1	15	15	—	—	140	1.0	本發明例
46	1	15	15	—	—	140	1.0	本發明例

[0182]

[Table 18]

表 18

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加 工 性	
35	○	△	△	◎	—	比較例
36	○	○	○	◎	—	本発明例
37	○	○+	○+	◎	—	本発明例
38	○	◎	◎	◎	—	本発明例
39	○	◎	◎	◎	—	本発明例
40	○	○	○	◎	—	本発明例
41	○	△	△	◎	—	比較例
42	○	◎	◎	◎	—	本発明例
43	○	◎	◎	◎	—	本発明例
44	○	◎	◎	◎	—	本発明例
45	○	◎	◎	◎	—	本発明例
46	○	◎	◎	◎	—	本発明例

[0183]

[Table 19]

表 19

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ) *3	(γ)/(β) *3	
*1	*2										
47	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
48	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
49	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
50	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
51	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
52	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
53	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
54	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
55	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
56	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例

[0184]

[Table 20]

表 20

No.	第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 温度 (℃)		膜厚 (μm)
		種類 *4	配合量 *5	種類 *6	配合量 *7			
47	1	15	15	—	—	140	0.001	比較例
48	1	15	15	—	—	140	0.1	本発明例
49	1	15	15	—	—	140	0.5	本発明例
50	1	15	15	—	—	140	0.7	本発明例
51	1	15	15	—	—	140	2.0	本発明例
52	1	15	15	—	—	140	2.5	本発明例
53	1	15	15	—	—	140	3.0	本発明例
54	1	15	15	—	—	140	4.0	本発明例
55	1	15	15	—	—	140	5.0	本発明例
56	1	15	15	—	—	140	20.0	比較例

[0185]

[Table 21]

表 21

No.	性 能					区 分
	外観	耐白錆性 CCT	アルカリ脱脂 後の耐白錆性 CCT	塗 装 密着性	加 工 性	
		50 サイクル後	50 サイクル後			
47	○	×	×	△	—	比較例
48	○	○—	○—	◎	—	本発明例
49	○	○	○	◎	—	本発明例
50	○	○+	○+	、◎	—	本発明例
51	○	◎	◎	◎	—	本発明例
52	○	◎	◎	◎	—	本発明例
53	○	◎	◎	◎	—	本発明例
54	○	◎	◎	◎	—	本発明例
55	○	◎	◎	◎	—	本発明例
56	○	◎	◎	◎	—	比較例 ※1

※1 溶接不可能

[0186]

[Table 22]

表 2 2

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					含 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
57	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
58	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
59	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
60	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
61	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
62	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
63	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
64	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
65	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
66	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例

[0187]

[Table 23]

表 2 3

No.	第二層皮膜							区 分
	樹 脂 組成物 *4	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 溫度 (℃)	膜厚 (μm)	
		種類 *5	配合量 *7	種類 *6	配合量 *7			
57	1	15	15	—	—	40	1.0	比較例
58	1	15	15	—	—	50	1.0	本發明例
59	1	15	15	—	—	80	1.0	本發明例
60	1	15	15	—	—	120	1.0	本發明例
61	1	15	15	—	—	180	1.0	本發明例
62	1	15	15	—	—	200	1.0	本發明例
63	1	15	15	—	—	230	1.0	本發明例
64	1	15	15	—	—	250	1.0	本發明例
65	1	15	15	—	—	350	1.0	本發明例
66	1	15	15	—	—	380	1.0	比較例

[0188]

[Table 24]

表 2 4

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	装 密着性	加工 性	
57	○	×	×	×	—	比較例
58	○	○—	○—	○	—	本発明例
59	○	○	○—	○+	—	本発明例
60	○	◎	○	◎	—	本発明例
61	○	◎	◎	◎	—	本発明例
62	○	◎	◎	◎	—	本発明例
63	○	◎	◎	◎	—	本発明例
64	○	◎	◎	◎	—	本発明例
65	○	◎	◎	◎	—	本発明例
66	○	△	△	◎	—	比較例

[0189]

[Table 25]

表 2 5

No.	め つき 鋼 板	第一層皮膜									区 分
		皮 膜 組成物	乾燥 温度 (℃)	膜厚 (μ m)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
67	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
68	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
69	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
70	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
71	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
72	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
73	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
74	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
75	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
76	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
77	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
78	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
79	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
80	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0190]

[Table 26]

表 26

No.	第二層皮膜						膜厚 (μ m)	区 分
	樹脂組成物 *4	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥温度 (℃)		
		種類 *5	配合量 *7	種類 *6	配合量 *7			
67	1	1	15	—	—	140	1.0	本発明例
68	1	2	15	—	—	140	1.0	本発明例
69	1	3	15	—	—	140	1.0	本発明例
70	1	4	15	—	—	140	1.0	本発明例
71	1	5	15	—	—	140	1.0	本発明例
72	1	6	15	—	—	140	1.0	本発明例
73	1	7	15	—	—	140	1.0	本発明例
74	1	8	15	—	—	140	1.0	本発明例
75	1	9	15	—	—	140	1.0	本発明例
76	1	10	15	—	—	140	1.0	本発明例
77	1	11	15	—	—	140	1.0	本発明例
78	1	12	15	—	—	140	1.0	本発明例
79	1	13	15	—	—	140	1.0	本発明例
80	1	14	15	—	—	140	1.0	本発明例

[0191]

[Table 27]

表 27

No.	性 能					区 分
	外観	耐白錆性 CCT	アルカリ脱脂 後の耐白錆性 CCT	塗 装 密着性	加 工 性	
		50 サイクル後	50 サイクル後			
67	○	○	○	◎	—	本発明例
68	○	○	○	◎	—	本発明例
69	○	○	○	◎	—	本発明例
70	○	○	○	◎	—	本発明例
71	○	○	○	◎	—	本発明例
72	○	○	○	◎	—	本発明例
73	○	○	○	◎	—	本発明例
74	○	○	○	◎	—	本発明例
75	○	○	○	◎	—	本発明例
76	○	○	○	◎	—	本発明例
77	○	○	○	◎	—	本発明例
78	○	○+	○+	◎	—	本発明例
79	○	○+	○+	◎	—	本発明例
80	○	○+	○+	◎	—	本発明例

[0192]

[Table 28]

表 28

No.	め つき 鋼板 *1	第一層皮膜									区 分
		皮 膜 組成物 *2	乾燥 温度 (℃)	膜厚 (μm)	皮膜付着量 *3				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ) *3	(γ)/(β) *3	
82	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
83	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
84	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
85	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
86	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
87	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88a	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88b	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88c	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88d	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88e	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88f	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
88g	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
89	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
90	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0193]

[Table 29]

表 29

No.	. 第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 温度		膜厚 (μm)
		種類 *4	配合量 *7	種類 *6	配合量 *7			
82	1	16	15	—	—	140	1.0	本発明例
83	1	17	15	—	—	140	1.0	本発明例
84	1	18	15	—	—	140	1.0	本発明例
85	1	19	15	—	—	140	1.0	本発明例
86	1	20	15	—	—	140	1.0	本発明例
87	1	21	15	—	—	140	1.0	本発明例
88a	1	1	15	1	10	140	1.0	本発明例
88b	1	5	15	1	10	140	1.0	本発明例
88c	1	7	15	1	10	140	1.0	本発明例
88d	1	12	15	1	10	140	1.0	本発明例
88e	1	13	15	1	10	140	1.0	本発明例
88f	1	14	15	1	10	140	1.0	本発明例
88g	1	15	15	1	10	140	1.0	本発明例
89	1	1	15	2	10	140	1.0	本発明例
90	1	1	15	3	10	140	1.0	本発明例

[0194]

[Table 30]

表 30

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加 工 性	
82	○	○+	○+	◎	—	本発明例
83	○	○+	○+	◎	—	本発明例
84	○	○+	○+	◎	—	本発明例
85	○	○+	○+	◎	—	本発明例
86	○	◎	◎	◎	—	本発明例
87	○	◎	◎	◎	—	本発明例
88a	○	○	○	◎	◎	本発明例
88b	○	○	○	◎	◎	本発明例
88c	○	○	○	◎	◎	本発明例
88d	○	○+	○+	◎	◎	本発明例
88e	○	○+	○+	◎	◎	本発明例
88f	○	○+	○+	◎	◎	本発明例
88g	○	◎	◎	◎	◎	本発明例
89	○	○	○	◎	◎	本発明例
90	○	○	○	◎	◎	本発明例

[0195]

[Table 31]

表 31

No.	め つ き 鋼 板	第一層皮膜									区 分
		皮 膜 組 成 物	乾燥 温度 (℃)	膜厚 (μ m)	皮膜付着量				皮膜成分のモル比		
					合 計 付 着 量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
91	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
92	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
93	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
94	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
95	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
96	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
97	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
98	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例

[0196]

[Table 32]

表 3 2

No.	第二層皮膜							区 分
	樹 脂 組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度	膜厚	
		種類 *4	配合量 *7	種類 *6	配合量 *7			
91	1	15	15	4	10	140	1.0	本發明例
92	1	15	15	5	10	140	1.0	本發明例
93	1	15	15	6	10	140	1.0	本發明例
94	1	15	15	1	1	140	1.0	本發明例
95	1	15	15	1	3	140	1.0	本發明例
96	1	15	15	1	40	140	1.0	本發明例
97	1	15	15	1	80	140	1.0	本發明例
98	1	15	15	1	100	140	1.0	比較例

[0197]

[Table 33]

表 3 3

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加工 性	
91	○	◎	◎	◎	◎	本発明例
92	○	◎	◎	◎	◎	本発明例
93	○	◎	◎	○	◎	本発明例
94	○	◎	◎	◎	○	本発明例
95	○	◎	◎	◎	◎	本発明例
96	○	◎	◎	◎	◎	本発明例
97	○	◎	◎	○	◎	本発明例
98	○	◎	◎	×	◎	比較例

[0198]

[Table 34]

表 3 4

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物 *1	膜 厚 (μ m)	皮膜付着量 *3				皮膜成分のモル比			
				乾燥温度 (℃)	合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)／(γ)	(γ)／(β)	
									*3	*3	
99	1	1	140	0.001	1.2	0.5	0.5	0.2	3.0	0.5	比較例
100	1	1	140	0.005	6	2.5	2.5	1	3.0	0.5	本発明例
101	1	1	140	0.01	12	5	5	2	3.0	0.5	本発明例
102	1	1	140	0.1	120	51	54	15	3.0	0.5	本発明例
103	1	1	140	0.5	599	250	272	77	3.0	0.5	本発明例
104	1	1	140	1.0	1197	500	544	153	3.0	0.5	本発明例
105	1	1	140	2	2395	1000	1089	306	3.0	0.5	本発明例
106	1	1	140	3	3591	1500	1633	458	3.0	0.5	本発明例
107	1	1	140	5	5986	2500	2722	764	3.0	0.5	比較例

[0199]

[Table 35]

表 3 5

No.	樹 脂 組 成 物	第二層皮膜						区 分
		防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 溫度	膜厚	
		種類 *4	配合量 *5	種類 *6	配合量 *7			
99	1	15	15	—	—	140	1.0	比較例
100	1	15	15	—	—	140	1.0	本發明例
101	1	15	15	—	—	140	1.0	本發明例
102	1	15	15	—	—	140	1.0	本發明例
103	1	15	15	—	—	140	1.0	本發明例
104	1	15	15	—	—	140	1.0	本發明例
105	1	15	15	—	—	140	1.0	本發明例
106	1	15	15	—	—	140	1.0	本發明例
107	1	15	15	—	—	140	1.0	比較例

[0200]

[Table 36]

表 3 6

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT ^{※1} 50 サイクル後	塗 装 密着性	加 工 性	
99	○	×	×	◎	—	比較例
100	○	○—	○—	◎	—	本発明例
101	○	○	○	◎	—	本発明例
102	○	○+	○+	◎	—	本発明例
103	○	◎	◎	◎	—	本発明例
104	○	◎	◎	◎	—	本発明例
105	○	◎	◎	◎	—	本発明例
106	○	◎	◎	◎	—	本発明例
107	○	◎	◎	◎	—	比較例

※ 1

※ 1 溶接が不可能

[0201]

[Table 37]

表 3 7

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度	膜厚	皮膜付着量				皮膜成分のモル比		
					合 計付着量	成分(α)	成分(β)	成分(γ)	(α)/(γ)	(γ)/(β)	
	*1	*2	(℃)	(μ m)	(mg/m ²)	(mg/m ²)	(mg/m ²)	(mg/m ²)	*3	*3	
108	1	1	30	0.3	359	150	163	46	3.0	0.5	比較例
109	1	1	50	0.3	359	150	163	46	3.0	0.5	本発明例
110	1	1	80	0.3	359	150	163	46	3.0	0.5	本発明例
111	1	1	120	0.3	359	150	163	46	3.0	0.5	本発明例
112	1	1	180	0.3	359	150	163	46	3.0	0.5	本発明例
113	1	1	200	0.3	359	150	163	46	3.0	0.5	本発明例
114	1	1	300	0.3	359	150	163	46	3.0	0.5	本発明例
115	1	1	350	0.3	359	150	163	46	3.0	0.5	比較例

[0202]

[Table 38]

表 3 8

No.	第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度		膜厚
		種類 *5	配合量 *7	種類 *6	配合量 *7			
108	1	15	15	—	—	140	1.0	比較例
109	1	15	15	—	—	140	1.0	本発明例
110	1	15	15	—	—	140	1.0	本発明例
111	1	15	15	—	—	140	1.0	本発明例
112	1	15	15	—	—	140	1.0	本発明例
113	1	15	15	—	—	140	1.0	本発明例
114	1	15	15	—	—	140	1.0	本発明例
115	1	15	15	—	—	140	1.0	比較例

[0203]

[Table 39]

表 3 9

No.	性 能					区 分
	外観	耐白錆性 CCT 50 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 50 サイクル後	塗 装 密着性	加 工 性	
108	○	×	×	×	—	比較例
109	○	○—	○—	○	—	本発明例
110	○	◎	◎	◎	—	本発明例
111	○	◎	◎	◎	—	本発明例
112	○	◎	◎	◎	—	本発明例
113	○	◎	◎	◎	—	本発明例
114	○	◎	◎	◎	—	本発明例
115	○	×	×	◎	—	比較例

[0204] In order to obtain [example 2] household electric appliances, building materials, and the organic covering steel plate for autoparts, Board thickness : The plating steel plate shown in Table 1 which performed various zinc system plating or aluminum system plating to cold rolled sheet steel (0.8mm and surface roughness Ra:1.0micrometer) is used as a processing negative. After alkaline-degreasing-processing and rinsing drying the front face of this plating steel plate, stoving of the processing liquid (coat constituent) shown in Table 2 and 3 was applied and carried out by the roll coater, and the 1st layer coat was made to form. The solid content (heating residue) or the spreading conditions of processing liquid (rolling force of a roll, rotational speed, etc.) adjusted the coating weight of this 1st layer coat. Subsequently, applied the coating constituent shown in Table 4 by the roll coater, it carried out stoving, the 2nd layer coat was made to form, and the organic covering steel plate of the example of this invention and the example of a comparison was manufactured. The solid content (heating residue) or the spreading conditions of a coating constituent (rolling force of a roll, rotational speed, etc.) adjusted the coating weight of the 2nd layer coat.

[0205] About the obtained organic covering steel plate, the quality engine performance (a coat appearance, white-rust-proof, the white-rust-proof after alkaline degreasing, coating adhesion,

workability, spot welding nature, conductivity) was evaluated. The result is shown in Table 40 - 57 with the coat configuration of the 1st layer coat and the 2nd layer coat etc. Evaluation of the spot welding nature of an organic covering steel plate and conductivity was performed by [as being the following], and made evaluation of other engine performance be the same as that of [an example 1].

[0206] (6) Using the test piece of 1.2mm of spot welding nature board thickness, under an upper electrode CR mold (16mm of diameters of former, 5.4mm of diameters of a tip), a bottom electrode female mold (16mm of diameters of a tip), the welding pressure of 300kg, and the conditions of the 13 cycle (60Hz) resistance welding time, the continuation RBI trial of spot welding nature was performed, the case where the diameter of a nugget became smaller than 4.4mm was made into the limitation of a welding RBI, and the following estimated.

O 1000 or more 3000 or more :RBI [continuation] O:continuation RBIs, 500 or more less than 3000 point **:continuation RBIs, below 1000 point x : less than 500 continuation RBIs [0207] (7)

Conductivity (surface-electrical-resistance value)

Using 4 probe resistivity meter ("RORESUTA AP" by Mitsubishi Chemical), the surface electrical resistance of a test piece was measured and the following estimated.

O 10 - 4 or less ohm [of :surface-electrical-resistance values] O:surface-electrical-resistance value 10-4ohm **, 10 - 3 or less ohm **:surface-electrical-resistance value 10-3ohm **, and less than [102ohm] x : surface-electrical-resistance value ** of 102ohms [0208] In following Table 40 - 57, *1-*7 indicated to front Naka show the following contents.

*1: The plating steel plate No given in Table 1

*2: The constituent No for the 1st layer coats given in Table 2 and 3

*3: A component (beta) is the coating weight of 2OP5 conversion, and a component (gamma) is the resin constituent No for the 2nd layer coats given in the coating weight *4:table 4 of the amount conversion of metals of Mg, Mn, and aluminum.

*5: The rust-proofing addition component No given in Table 5

*6: Solid lubricant No given in Table 6

*7: Loadings to the solid content 100 weight section of a resin constituent (weight section)

[0209]

[Table 40]

表 40

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (°C)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ) *3	(γ)/(β) *3	
1	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
2	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
3	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
4	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
5	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
6	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
7	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
8	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
9	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
10	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
11	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0210]

[Table 41]

表 4 1

No.	第二層皮膜							区 分
	樹脂組成物 *4	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥温度 (℃)	付着量 (g/m ²)	
		種類 *5	配合量 *7	種類 *6	配合量 *7			
1	1	15	15	—	—	140	0.3	本発明例
2	2	15	15	—	—	140	0.3	本発明例
3	3	15	15	—	—	140	0.3	本発明例
4	4	15	15	—	—	140	0.3	本発明例
5	5	15	15	—	—	140	0.3	本発明例
6	6	15	15	—	—	140	0.3	本発明例
7	7	15	15	—	—	140	0.3	本発明例
8	8	15	15	—	—	140	0.3	本発明例
9	9	15	15	—	—	140	0.3	本発明例
10	10	15	15	—	—	140	0.3	本発明例
11	11	15	15	—	—	140	0.3	本発明例

[0211]

[Table 42]

表 4 2

No.	性 能							区 分
	外観	耐白錆性 CCT 20 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 20 サイクル後	塗 装 密着性	溶 接 性	導 電 性	加 工 性	
1	○	◎	◎	◎	◎	◎	—	本発明例
2	○	◎	◎	◎	◎	◎	—	本発明例
3	○	◎	◎	◎	◎	◎	—	本発明例
4	○	◎	◎	◎	◎	◎	—	本発明例
5	○	◎	◎	◎	◎	◎	—	本発明例
6	○	◎	◎	◎	◎	◎	—	本発明例
7	○	◎	◎	◎	◎	◎	—	本発明例
8	○	◎	◎	◎	◎	◎	—	本発明例
9	○	◎	◎	◎	◎	◎	—	本発明例
10	○	◎	◎	◎	◎	◎	—	本発明例
11	○	◎	◎	◎	◎	◎	—	本発明例

[0212]

[Table 43]

表 4 3

No.	め つき 鋼 板	第一層皮膜									区 分
		皮 膜 組成物	乾燥 温度 (℃)	膜厚 (μ m)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
12	1	2	140	0.3	344	30	245	69	0.4	0.5	本発明例
13	1	3	140	0.3	363	90	245	28	3.0	0.2	本発明例
14	1	4	140	0.3	360	200	99	61	3.0	1.1	本発明例
15	1	5	140	0.3	358	290	53	15	18.0	0.5	本発明例
16	1	6	140	0.3	600	150	163	46	3.0	0.5	本発明例
17	1	7	140	0.3	358	160	174	24	3.0	0.5	本発明例
18	1	8	140	0.3	360	35	286	39	0.4	0.5	本発明例
19	1	9	140	0.3	349	90	245	14	3.0	0.2	本発明例
20	1	10	140	0.3	362	220	109	33	3.0	1.1	本発明例
21	1	11	140	0.3	362	300	54	8	18.0	0.5	本発明例
22	1	12	140	0.3	358	160	174	24	3.0	0.5	本発明例
23	1	13	140	0.3	355	160	174	21	3.0	0.5	本発明例

[0213]

[Table 44]

表 4 4

No.	第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 温度 (℃)		付着量 (g/m ²)
		種類 *4	配合量 *5	種類 *6	配合量 *7			
12	1	15	15	—	—	140	0.3	本發明例
13	1	15	15	—	—	140	0.3	本發明例
14	1	15	15	—	—	140	0.3	本發明例
15	1	15	15	—	—	140	0.3	本發明例
16	1	15	15	—	—	140	0.3	本發明例
17	1	15	15	—	—	140	0.3	本發明例
18	1	15	15	—	—	140	0.3	本發明例
19	1	15	15	—	—	140	0.3	本發明例
20	1	15	15	—	—	140	0.3	本發明例
21	1	15	15	—	—	140	0.3	本發明例
22	1	15	15	—	—	140	0.3	本發明例
23	1	15	15	—	—	140	0.3	本發明例

[0214]

[Table 45]

表 4 5

No.	性 能							区 分
	外観	耐白錆性 CCT 20 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 20 サイクル後	塗 装 密着性	溶 接性	導 電性	加 工性	
12	○	◎	◎	◎	◎	◎	—	本発明例
13	○	◎	◎	◎	◎	◎	—	本発明例
14	○	◎	◎	◎	◎	◎	—	本発明例
15	○	◎	◎	◎	◎	◎	—	本発明例
16	○	◎	◎	◎	◎	◎	—	本発明例
17	○	◎	◎	◎	◎	◎	—	本発明例
18	○	◎	◎	◎	◎	◎	—	本発明例
19	○	◎	◎	◎	◎	◎	—	本発明例
20	○	◎	◎	◎	◎	◎	—	本発明例
21	○	◎	◎	◎	◎	◎	—	本発明例
22	○	○+	○+	◎	◎	◎	—	本発明例
23	○	○	○	○	◎	◎	—	本発明例

[0215]

[Table 46]

表 4 6

No.	め つき 鋼 板	第一層皮膜									区 分
		皮 膜 組成物	乾燥 温度 (℃)	膜厚 (μ m)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
24	1	1	140	0.3	359	150	163	46	3.0	0.5	比較例
25	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
26	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
27	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
28	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
29	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
30	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
31	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0216]

[Table 47]

表 4 7

No.	第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度 (℃)		付着量 (g/m ²)
		種類 *4	配合量 *7	種類 *6	配合量 *7			
24	1	15	15	—	—	140	0.01	比較例
25	1	15	15	—	—	140	0.1	本発明例
26	1	15	15	—	—	140	0.15	本発明例
27	1	15	15	—	—	140	0.2	本発明例
28	1	15	15	—	—	140	0.3	本発明例
29	1	15	15	—	—	140	0.4	本発明例
30	1	15	15	—	—	140	0.49	本発明例
31	1	15	15	—	—	140	0.5	本発明例

[0217]

[Table 48]

表 4 8

No.	性 能							区 分
	外観	耐白錆性 CCT	アルカリ脱脂 後の耐白錆性 CCT	塗 装 密着性	溶 接 性	導 電 性	加 工 性	
		20 サイクル後	20 サイクル後					
24	○	×	×	△	◎	◎	—	比較例
25	○	○	○	◎	◎	◎	—	本発明例
26	○	◎	◎	◎	◎	◎	—	本発明例
27	○	◎	◎	◎	◎	◎	—	本発明例
28	○	◎	◎	◎	◎	◎	—	本発明例
29	○	◎	◎	◎	◎	◎	—	本発明例
30	○	◎	◎	◎	◎	◎	—	本発明例
31	○	◎	◎	◎	△	△	—	本発明例

[0218]

[Table 49]

表 49

No.	めつき鋼板	第一層皮膜									区 分
		皮 膜組成物	乾燥温度 (℃)	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ) *3	(γ)/(β) *3	
32	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
33	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
34	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
35	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
36	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
37	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
38	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
39	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
40	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
41	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
42	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
43	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
44	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
45	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0219]

[Table 50]

表 50

No.	第二層皮膜						区 分	
	樹 脂 組成物	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 温度 (℃)		付着量 (g/m ²)
		種類 *4	配合量 *5	種類 *6	配合量 *7			
32	1	1	15	—	—	140	0.3	本發明例
33	1	2	15	—	—	140	0.3	本發明例
34	1	3	15	—	—	140	0.3	本發明例
35	1	4	15	—	—	140	0.3	本發明例
36	1	5	15	—	—	140	0.3	本發明例
37	1	6	15	—	—	140	0.3	本發明例
38	1	7	15	—	—	140	0.3	本發明例
39	1	8	15	—	—	140	0.3	本發明例
40	1	9	15	—	—	140	0.3	本發明例
41	1	10	15	—	—	140	0.3	本發明例
42	1	11	15	—	—	140	0.3	本發明例
43	1	12	15	—	—	140	0.3	本發明例
44	1	13	15	—	—	140	0.3	本發明例
45	1	14	15	—	—	140	0.3	本發明例

[0220]

[Table 51]

表 5 1

No	性 能							区 分
	外観	耐白錆性 CCT 20 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 20 サイクル後	塗 装 密着性	溶 接 性	導 電 性	加 工 性	
32	○	○	○	◎	◎	◎	—	本発明例
33	○	○	○	◎	◎	◎	—	本発明例
34	○	○	○	◎	◎	◎	—	本発明例
35	○	○	○	◎	◎	◎	—	本発明例
36	○	○	○	◎	◎	◎	—	本発明例
37	○	○	○	◎	◎	◎	—	本発明例
38	○	○	○	◎	◎	◎	—	本発明例
39	○	○	○	◎	◎	◎	—	本発明例
40	○	○	○	◎	◎	◎	—	本発明例
41	○	○	○	◎	◎	◎	—	本発明例
42	○	○	○	◎	◎	◎	—	本発明例
43	○	○+	○+	◎	◎	◎	—	本発明例
44	○	○+	○+	◎	◎	◎	—	本発明例
45	○	○+	○+	◎	◎	◎	—	本発明例

[0221]

[Table 52]

表 5 2

No	めつき鋼板	第一層皮膜									区 分
		皮 膜 組 成 物 *1	膜 厚 乾 燥 温 度 (℃) *2	膜厚 (μm) *2	皮膜付着量				皮膜成分のモル比		
					合 計 付 着 量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
46	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
47	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
48	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
49	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
50	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
51	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例
52	1	1	140	0.3	359	150	163	46	3.0	0.5	本発明例

[0222]

[Table 53]

表 5 3

No.	第二層皮膜						区 分	
	樹 脂 組 成 物 *4	防錆添加成分(Y)		固形潤滑剤(Z)		乾燥 温度 (℃)		付着量 (g/m ²)
		種類 *5	配合量 *7	種類 *6	配合量 *7			
46	1	16	15	—	—	140	0.3	本発明例
47	1	17	15	—	—	140	0.3	本発明例
48	1	18	15	—	—	140	0.3	本発明例
49	1	19	15	—	—	140	0.3	本発明例
50	1	20	15	—	—	140	0.3	本発明例
51	1	21	15	—	—	140	0.3	本発明例
52	1	15	15	1	10	140	0.3	本発明例

[0223]

[Table 54]

表 5 4

No.	性 能							区 分
	外観	耐白錆性 CCT 20 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 20 サイクル後	塗 装 密着性	溶 接 性	導 電 性	加 工 性	
46	○	○+	○+	◎	◎	◎	—	本発明例
47	○	○+	○+	◎	◎	◎	—	本発明例
48	○	○+	○+	◎	◎	◎	—	本発明例
49	○	○+	○+	◎	◎	◎	—	本発明例
50	○	◎	◎	◎	◎	◎	—	本発明例
51	○	◎	◎	◎	◎	◎	—	本発明例
52	○	◎	◎	◎	◎	◎	◎	本発明例

[0224]

[Table 55]

表 5 5

No.	めつき 鋼板	第一層皮膜									区 分
		皮 膜 組成物	乾燥 温度	膜厚 (μm)	皮膜付着量				皮膜成分のモル比		
					合 計 付着量 (mg/m ²)	成分(α) (mg/m ²)	成分(β) (mg/m ²)	成分(γ) (mg/m ²)	(α)/(γ)	(γ)/(β)	
									*3	*3	
53	1	1	140	0.001	1.2	0.5	0.5	0.2	3.0	0.5	比較例
54	1	1	140	0.005	6	2.5	2.5	1	3.0	0.5	本発明例
55	1	1	140	0.01	12	5	5	2	3.0	0.5	本発明例
56	1	1	140	0.1	120	51	54	15	3.0	0.5	本発明例
57	1	1	140	0.5	599	250	272	77	3.0	0.5	本発明例
58	1	1	140	1.0	1197	500	544	153	3.0	0.5	本発明例

[0225]

[Table 56]

表 56

No.	第二層皮膜						区 分	
	樹脂組成物 *4	防錆添加成分 (Y)		固形潤滑剤 (Z)		乾燥 溫度 (℃)		付着量 (g/m ²)
		種類 *5	配合量 *7	種類 *6	配合量 *7			
53	1	15	15	—	—	140	0.3	比較例
54	1	15	15	—	—	140	0.3	本發明例
55	1	15	15	—	—	140	0.3	本發明例
56	1	15	15	—	—	140	0.3	本發明例
57	1	15	15	—	—	140	0.3	本發明例
58	1	15	15	—	—	140	0.3	本發明例

[0226]

[Table 57]

表 57

No.	性 能							区 分
	外観	耐白錆性 CCT 20 サイクル後	アルカリ脱脂 後の耐白錆性 CCT 20 サイクル後	塗 装 密着性	溶 接 性	導 電 性	加 工 性	
53	○	×	×	◎	◎	◎	—	比較例
54	○	○—	○—	◎	◎	◎	—	本発明例
55	○	○	○	◎	◎	◎	—	本発明例
56	○	○+	○+	◎	◎	◎	—	本発明例
57	○	◎	◎	◎	◎	◎	—	本発明例
58	○	◎	◎	◎	△	△	—	本発明例

[0227]

[Effect of the Invention] As stated above, moreover, the organic covering steel plate of this invention has corrosion resistance advanced as an organic covering steel plate of the application of building materials, household electric appliances, an automobile, etc. in the coat component of the processing liquid at the time of manufacture, or a product, excluding hexavalent chromium at all, and is excellent in a coat appearance, coating adhesion, etc. Moreover, the organic covering steel plate which has the outstanding corrosion resistance suitable as materials, such as OA equipment with which advanced spot welding nature is demanded, and an AV equipment, advanced conductivity, and spot welding nature can be obtained from the need of severe conductivity being required from the cure against a noise of a product, and acquiring high productivity in the assembly process of a chassis etc., by regulating the coating weight of the 1st layer coat and the 2nd layer coat in the specific range.

[Translation done.]